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Syntheses of Twelve-Membered Ring Titana- and Zirconasiloxane Compounds and Their Properties as Ceramic Precursor

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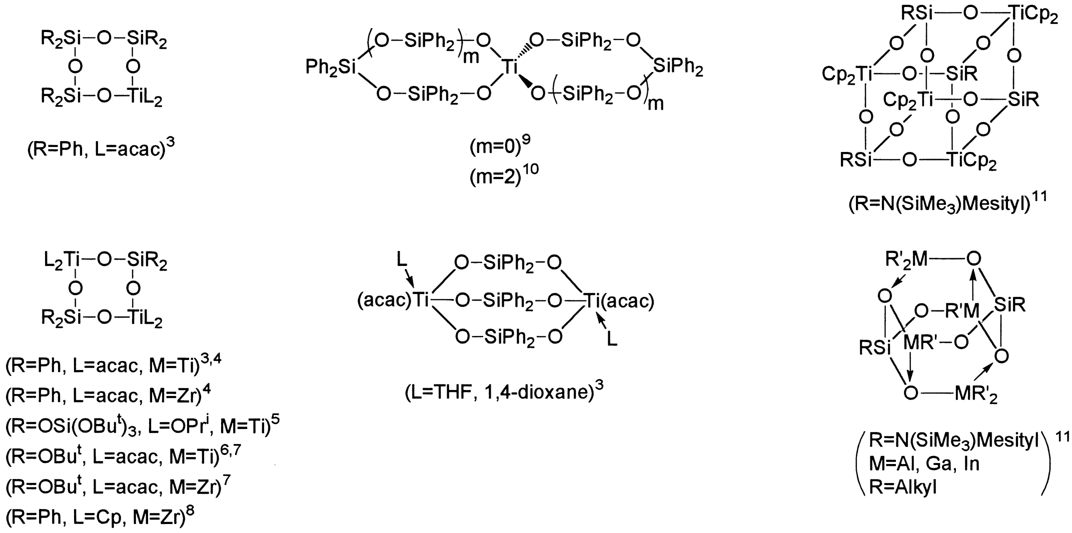
Cyclic metallasiloxanes, $[(SiR^1R^2O)_2M(acac)_2O]_2$ (R^1 = Me, R^2 = OBu^t; R^1 = R^2 = OBu^t; R^1 = OPr^i, R^2 = OBu^t; M = Ti, Zr), were synthesized by the reaction of disiloxane-1,3-diols with diisopropoxidobis(2,4-pentanedionato)titanium(IV) or diisopropoxidobis(2,4-pentanedionato)zirconium(IV) in tetrahydrofuran. Cyclic titanasiloxanes and zirconasiloxanes have twelve-membered rings with the $(Si–O–Si–O–Ti–O)_2$ linkages and $(Si–O–Si–O–Zr–O)_2$ linkages, respectively. The pyrolysis of cyclic titanasiloxanes and zirconasiloxanes provided $2SiO_2–TiO_2$ and $2SiO_2–ZrO_2$ ceramics, respectively, which consist of amorphous silica and crystallized titania or zirconia.

Metallasiloxane and polymetallasiloxane compounds are potential precursors as oxide ceramics in modern chemical industries, since ceramic materials are easily prepared by the pyrolysis of precursors fabricated in the forms of fibers, thin films, and bulk bodies[1]. This process is known as the precursor method or the sol-gel process and can be applied to the preparation of single- or multi-component ceramic materials via three steps: syntheses of precursor polymers, molding, and pyrolysis. Therefore, the synthesis of precursor polymers with high processability is a key step in the preparation of ceramic materials with preferable performance.

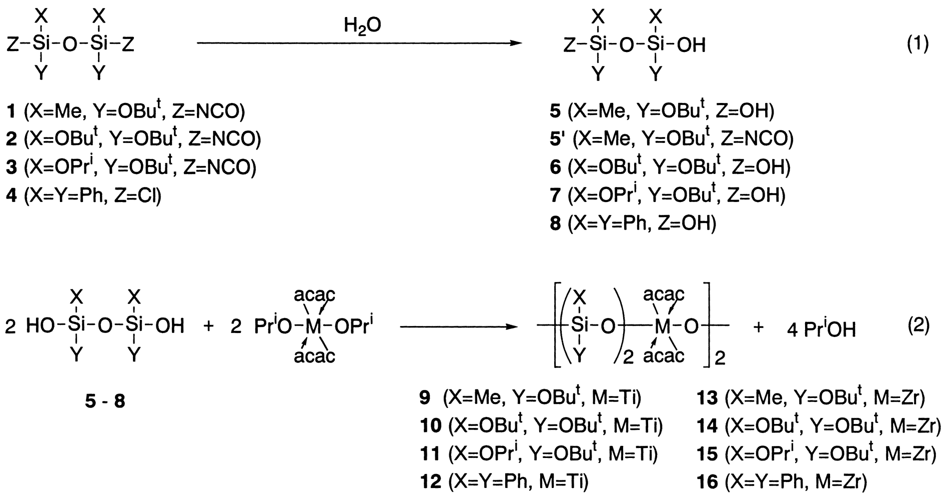
Metallasiloxane bondings, which include a main chain of metallasiloxane and polymetallasiloxane compounds, are formed simply by the following[2]: 1) hydrolysis of sila- and metalla-functionalized materials, 2) polycondensation between sila- and metalla-functionalized materials, and 3) oxidation of silicon-metal bondings. Among these three processes, the hydrolysis of sila- and metalla-functionalized materials is most preferable because of the big availability in the selection of starting materials such as metal alkoxides, metal chlorides, and metal acetates. Such processes, however, often provide an obstacle to the microstructural control of the precursors to provide random block copolymers composed of siloxane bonds (–Si–O–Si–) and metalloxane bonds (–M–O–M–).

The heterofunctional condensation reaction between silanols with metal chelate compounds is a preferable process to prepare metallasiloxane compounds with a well-defined backbone structure, as shown in Scheme 1: Eight-membered ring metallasiloxane oligomers[3–8], spiro titanasiloxanes[9,10], bicyclic titanasiloxanes[3], and cage-type metallasiloxanes[11].

On the synthesis of metallasiloxane oligomers, the condensation rates and the thermodynamic stability must be con-



Scheme 1.



1 (X=Me, Y=OBu^t, Z=NCO)
2 (X=OBu^t, Y=OBu^t, Z=NCO)
3 (X=OPr^i, Y=OBu^t, Z=NCO)
4 (X=Y=Ph, Z=Cl)

5 (X=Me, Y=OBu^t, Z=OH)
5' (X=Me, Y=OBu^t, Z=NCO)
6 (X=OBu^t, Y=OBu^t, Z=OH)
7 (X=OPr^i, Y=OBu^t, Z=OH)
8 (X=Y=Ph, Z=OH)

9 (X=Me, Y=OBu^t, M=Ti)
10 (X=OBu^t, Y=OBu^t, M=Ti)
11 (X=OPr^i, Y=OBu^t, M=Ti)
12 (X=Y=Ph, M=Ti)

13 (X=Me, Y=OBu^t, M=Zr)
14 (X=OBu^t, Y=OBu^t, M=Zr)
15 (X=OPr^i, Y=OBu^t, M=Zr)
16 (X=Y=Ph, M=Zr)

Chart 1.

Table 1. Abbrebiation and Structure of Compound, $[(\mathrm{SiXYO})_2\mathrm{M(acac)}_2\mathrm{O}]_2$

Compd	Structure of groups			Compd	Structure of groups		
	M	**X**	**Y**		**M**	**X**	**Y**
9	Ti	Me	OBu^t	**13**	Zr	Me	OBu^t
10	Ti	OBu^t	OBu^t	**14**	Zr	OBu^t	OBu^t
11	Ti	OPr^i	OBu^t	**15**	Zr	OPr^i	OBu^t
12	Ti	Ph	Ph	**16**	Zr	Ph	Ph

Table 2. Results on the Hydrolysis of **1**[a)]

No.	Molar ratio Et_3N/**1**	Reflux time/h	Relative yield by GC/%			
			1	**5′**	**5**	Others
1	0	3	94	1	0	5
2	0.1	3	0	54	37	9
3	2	0	0	60	33	7
4	2	1	0	13	80	7
5	2	3	0	4	86	10

a) Scale of operation: **1**, 6.64 g (0.02 mol); water 0.72 g (0.04 mol); triethylamine 4.00 g (0.04 mol). Solvent: THF (10 mL). They were mixed at 0 °C then refluxed for certain period.

sidered carefully to produce a main product with a desirable metal composition and configuration: the steric hindrance around silicon and metal atoms results in a metal composition of metallasiloxane oligomers of Si/M = 1, while the lower steric hindrance and/or a rapid self-condensation of silanol gives rise to a metal composition of more than one. Therefore, the metal composition of metallasiloxane oligomers has been Si/M = 1, 3, 4, and 8, but not Si/M = 2.

Cyclic metallasiloxanes with a metal composition of Si/M = 2, which has a twelve-membered ring system rather than a six-membered ring, would be prepared by designing the condensation reaction between disiloxanediols with metal chelate compounds. In this paper, the syntheses of cyclic metallasiloxanes with a composition of Si/Ti = 2 or Si/Zr = 2 will be reported according to reaction 1 and 2 in Chart 1. The abbreviations and structures of compounds are summarized in Table 1.

Results and Discussion

Synthesis of Disiloxane-1,3-diols. The hydrolysis of 1,3-diisocyanato disiloxanes **1**, **2** and **3** was carried out by adding water to the solution of these compounds to depress the further hydrolysis of products. Results for the hydrolysis of **1** are summarized in Table 2. The hydrolysis in the absence of triethylamine (No. 1) led to the recovery of **1**. The hydrolysis of **1** in the presence of triethylamine (No. 2) provided 1,3-di-*t*-butoxy-3-isocyanato-1,3-dimethyldisiloxanols **5′** and **5**. The increasing triethylamine (No. 3, 4, 5) accelerated the hydrolysis of isocyanato group, which is based on the rapid condensation of isocyanic acid to cyanuric acid to result in the transferring of equilibrium in the direction of the products. The hydrolysis of **1** proceeded stepwisely via **5′** as an intermediate. The hydrolysis of **5′** was also accelerated by increasing the amount of triethylamine and the reflux time. Unfortunately, the isolation of **5′** was unsuccessful by fractional distillation or recrystallization because **5′** has a boiling point close to that of **5** and was very soluble in common organic solvents. Compound **5** was isolated by recrystallization in 78.9% yield. Compounds **6** and **7** were synthesized from **2** and **3**, respectively, based on the same procedure.

The structural isomers are expected for **5** and **7**, but the separation and isolation of isomers were not possible by conventional techniques such as fractional crystallization and column chromatography.

On the other hand, **8** was synthesized according to the literature[12] by a simple hydrolysis of **4** followed by recrystallization.

Synthesis of Cyclic Titanasiloxanes and Cyclic Zirconasiloxanes. The reaction of **5** with diisopropoxidobis(2,4-pentanedionato)titanium(IV) (PTP) was examined to produce an alternative oligotitanasiloxane. The progress of this reaction was monitored by gas chromatography analysis; the reaction resulted in the formation of isopropyl alcohol in quantitative yield. The evaporation of isopropyl alcohol and tetrahydrofuran (THF) and following reprecipitation with THF and hexane provided cyclic titanasiloxane **9** as yellowish white powder, which decomposes at 162.4 °C without melting.

Table 3. T_g^5, T_g^{50}, Ceramic Yield of Cyclic Metallosiloxanes and Crystallization Temperature

Compound	$T_g^{5a)}$/°C	$T_g^{50b)}$/°C	Ceramic yield/%	Crystallization
			Found (Calcd)$^{c)}$	temperature$^{d)}$/°C
9	180	430	38.8 (38.0)	700–750
10	190	270	31.0 (31.2)	700–750
11	190	280	33.0 (32.6)	700–750
12	210	410	30.8 (30.4)	700–750
13	150	430	43.0 (42.7)	800–850
14	190	290	35.3 (35.5)	800–850
15	190	350	37.5 (36.9)	800–850
16	250	410	34.6 (34.7)	800–850

a) Temperature at the 5% weight loss was observed.

b) Temperature at the 50% weight loss was observed.

c) Determined by means of thermogravimetry based on the residual weight at 1400 °C. Calcd. value based on the formula of $2SiO_2$–MO_2 is shown in the parentheses.

d) Determined based on the X-ray diffractograms.

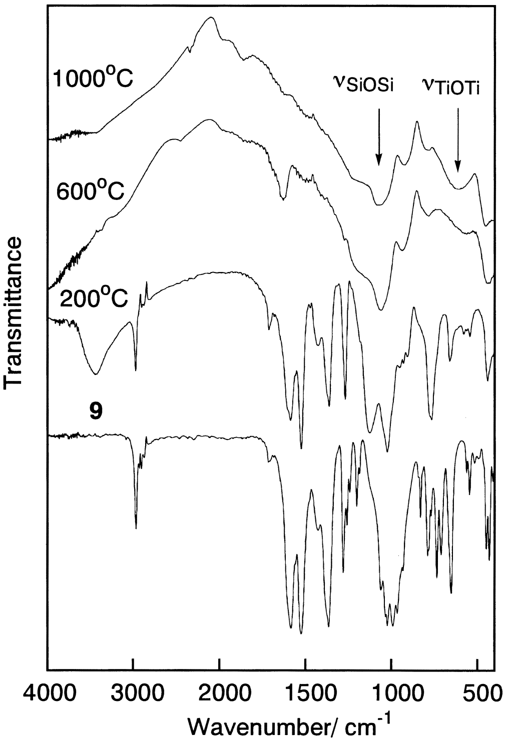


Fig. 1. IR spectra of **9** on pyrolysis under air atmosphere (KBr disk method).

The structure of **9** was identified by nuclear magnetic resonance (NMR), infrared (IR) and mass (MS) spectra: ^{1}H NMR spectrum showed the signals due to *t*-butoxy ($\delta = 1.28$ ppm), silylmethyl ($\delta = 0.10$ ppm) and acac ($\delta = 2.00$ and 5.60 ppm) groups with a reasonable proton ratio, while no signals due to silanol and isopropoxy groups were observed. ^{13}C NMR spectrum showed the signals due to *t*-butoxy ($\delta = 31.6$ and 72.7 ppm), silylmethyl ($\delta = -2.64$ ppm) and acac ($\delta = 25.4$, 26.9, 104.4, 186.5, and 192.7 ppm) groups. Two sets of signals were observed for the methyl and carbonyl groups in acac; these are often observed for the other cyclic titanasiloxanes **10–12**. Since titanium atom is crowded with acac and siloxy groups to form a six-folded conformation, the two methyl and carbonyl groups in an acac group are placed in unequivalent magnetic fields. ^{29}Si NMR spectrum indicated a signal ($\delta = -55.7$ ppm), which suggests a unique environment of the silicon atom. The IR spectrum showed an absorption peak $\nu_{Si\text{-}O\text{-}Ti}$ but no absorption peak ν_{OH}. A molecular ion was observed on the MS analysis at $m/z = 1052$. These spectral data support the assignment of the structure of cyclic titanasiloxane **9** as $\{[SiMe(OBu^t)O]_2Ti(acac)_2O\}_2$.

The other cyclic titanasiloxanes **10–12** were synthesized by the same procedure in high yields and characterized to be cyclic compounds bearing a twelve-membered ring of titanasiloxane.

Similarly, **13–16** were synthesized by the reaction of disiloxanediols **5–8** with diisopropoxidobis(2,4-pentanedionato)zirconium(IV) (PZP). These cyclic zirconasiloxanes were isolated in high yields as pale yellow powders. The formation of cyclic zirconasiloxanes was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR and MS spectra, each was found to be composed of a twelve-membered ring of zirconasiloxane (Si–O–Si–O–Zr–O)$_2$.

Pyrolysis of Cyclic Titanasiloxanes. The pyrolyzing process of **9–12** under air atmosphere was monitored by thermogravimetric (TG) analysis. As shown in Table 3, T_g^5s were 180 °C (**9**), 190 °C (**10**), 190 °C (**11**), and 210 °C (**12**), while T_g^{50}s were 430 °C (**9**), 270 °C (**10**), 280 °C (**11**), and 410 °C (**12**). The lowest T_g^5 and highest T_g^{50} for **9** indicates the lower and higher heat-stabilities of *t*-butoxy and silylmethyl groups, respectively. The rapid weight loss, observed for **10** and **11**, supports the combustion of alkoxy groups with an evolution of isobutene or propene on heating. On the other hand, the relatively high T_g^5 and T_g^{50} for **12** suggests the slower decomposition of silylphenyl group. The residual weights, or ceramic yields, at 1400 °C for **9–12** agreed with the calculated ones to suggest the formation of $2SiO_2$–TiO_2 ceramic materials by a conventional pyrolysis without evaporation or sublimation of the precursor.

The IR spectra of **9** on pyrolysis are shown in Fig. 1. The IR spectrum of **9** indicates absorption peaks due to acac, *t*-butoxy, and silylmethyl groups in addition to Si–O–Si and Si–O–Ti

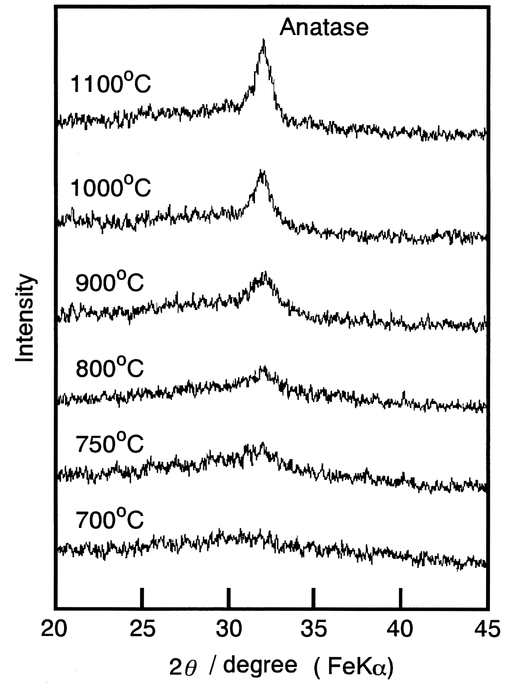


Fig. 2. X-ray diffractograms of **9** on pyrolysis under air atmosphere (Fe $K\alpha$).

linkages. On the pyrolysis at 200 °C, a new peak ν_{OH} (3400 cm^{-1}) was observed that suggests the formation of silanol by the elimination of isobutene. When the pyrolysis temperature was raised to 600 °C and 1000 °C, the absorption peaks due to $\nu_{Si\text{-}O\text{-}Si}$ (1000–1150 cm^{-1}), $\nu_{Si\text{–}O\text{–}Ti}$ (970–940 cm^{-1}), and $\nu_{Ti\text{–}O\text{–}Ti}$ (600 cm^{-1}) are clearly observed with a disappearance of the peaks due to organic groups. This spectral feature agrees with the TG profile and thus supports the ceramization process by elimination of isobutene and other organic groups.

The X-ray diffractograms of **9** on pyrolysis are shown in Fig. 2. The diffraction pattern was identified to be titania anatase form. The transformation of anatase to rutile form was not observed on pyrolysis at elevated temperature. The peak becomes sharper and the intensity increases as pyrolysis temperature rises, suggesting the progress of the crystallization of titania. The crystallization of the titanium component in **9** to titania (anatase form) was monitored by the diffraction pattern at $2\theta = 31.95°$. The crystallization temperature of **9** was determined to be 700–750 °C, because a broad diffraction pattern was observed on the pyrolysis at 750 °C but not at 700 °C. The crystalline size of titania (anatase form), as shown in Fig. 3, increased uniformly when the pyrolysis temperature was raised.

The crystallization temperature of titania was found to be dependent on the composition of silicon regardless of the side chain groups attached to silicon, as the crystallization of titania as $2SiO_2$–TiO_2 from **9–12** takes place at higher temperature than that from $[Si(OBu^t)_2OTi(acac)_2]_2$ which provided SiO_2–TiO_2 at 600-650 °C[13].

Pyrolysis of Cyclic Zirconasiloxanes. The pyrolyzing process of **13–16** under air atmosphere was monitored by TG analysis. As shown in Table 3, the same feature was observed for **13–16** on comparing the tendency of T_g^{5} and T_g^{50}. The observed ceramic yield, shown in Table 3, agreed with the calculated one for each compound, which suggests the formation of $2SiO_2$-ZrO_2 ceramic material by a pyrolysis without evaporation or sublimation of the precursors.

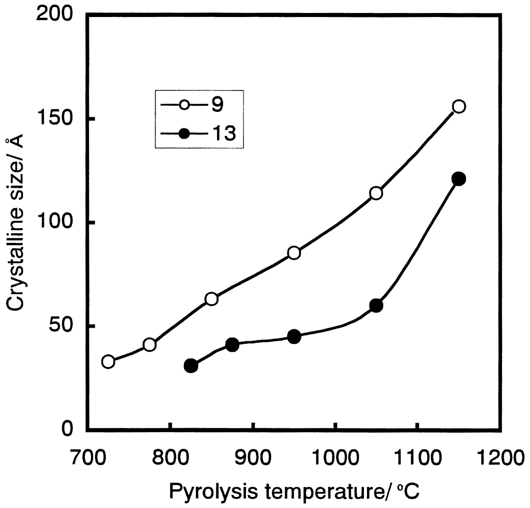


Fig. 3. Crystalline size of titania and zirconia on pyrolysis of **9** and **13** under air atmosphere.

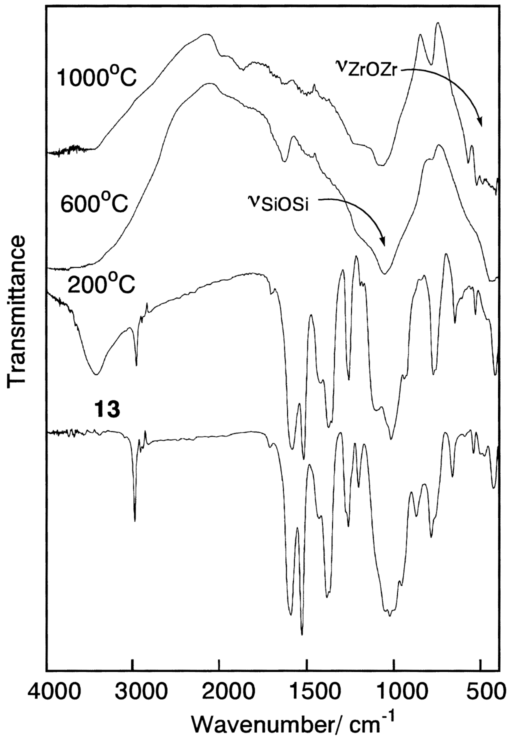


Fig. 4. IR spectra of **13** on pyrolysis under air atmosphere (KBr disk method).

On tracing the pyrolysis process of **13** by IR spectra as shown in Fig. 4, a new peak ν_{OH} (3400 cm^{-1}) appeared at 200 °C; this was caused by an elimination of isobutene. When **13** was pyrolyzed at 600°C, the absorption peaks due to $\nu_{Si\text{–}O\text{–}Si}$ (1000–1150 cm^{-1}), $\nu_{Si\text{–}O\text{–}Zr}$ (970–940 cm^{-1}), and $\nu_{Zr\text{–}O\text{–}Zr}$ (420 cm^{-1}) were clearly observed with a disappearance of the peaks due to organic groups.

The X-ray diffractograms of **13** on pyrolysis are shown in

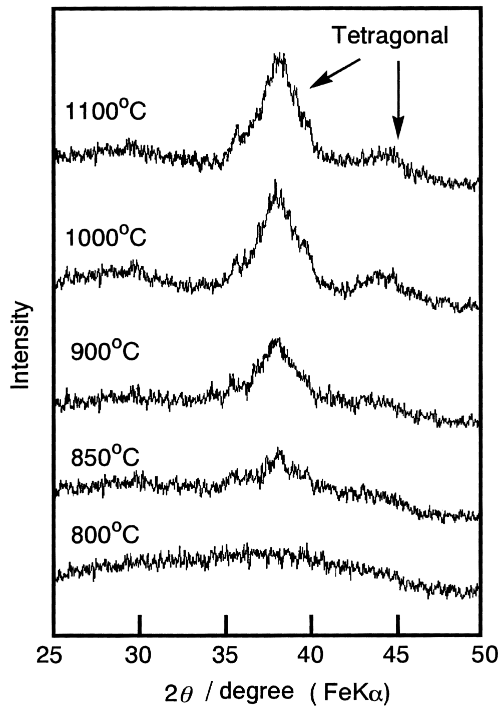


Fig. 5. X-Ray diffractograms of **13** on pyrolysis under air atmosphere (Fe *Kα*).

Fig. 5. The crystallization of the zirconium component in **13** to zirconia (tetragonal form) was monitored by the diffraction pattern at $2\theta = 38.20°$. The crystallization temperature of **13** was determined to be 800–850 °C. The crystallization temperatures of **14**–**16** were 800–850 °C, as shown in Table 3. The crystallization process of **14**–**16** was similar to that of **13**.

The crystalline size of zirconia (tetragonal form) is displayed in Fig. 3. With raising pyrolysis temperature, the crystalline size increased uniformly, while the crystalline size of zirconia was smaller than that of titania. As expected from the atomic sizes of titanium and zirconium, the coagulation of zirconia at lower pyrolysis temperature is slower than that of titania, which results in the rise in the crystallization temperature and in the crystalline size of zirconia becoming smaller than that of titania.

Experimental

Materials. 1,3-Di-*t*-butoxy-1,3-diisocyanato-1,3-dimethyldisiloxane[14] (**1**), di-*t*-butoxydiisocyanatosilane[15], *t*-butoxy(isopropoxy)diisocyanatosilane[16], 1,1,3,3-tetraphenyldisiloxanediol[12] (**8**), diisopropoxidobis(2,4-pentanedionato)titanium(IV)[17] (PTP) and diisopropoxidobis(2,4-pentanedionato)zirconium(IV)[18] (PZP) were synthesized according to the literature.

Other chemicals such as tetrahydrofuran (THF), pentane, hexane and triethylamine were purified by a conventional method before use.

Synthesis of 1,3-Di-*t*-butoxy-1,3-dimethyldisiloxanediol (5). A THF solution (100 mL) containing water (0.72 g, 0.04 mol) and triethylamine (4.00 g, 0.04 mol) was added dropwise to the THF (10 mL) solution of **1** (6.64 g, 0.02 mol) at 0 °C. After reflux for 24 h, cyanuric acid was filtered. The filtrate was concentrated and hexane (50 mL) was added to precipitate cyanuric acid again. After filtration of cyanuric acid, the filtrate was concentrated and then dissolved to pentane to recrystallize **5**. Compound **5** was isolated as a white powder by the filtration and drying under reduced pressure.

5 Yield: 78.9%. Mp 90.7–91.3 (decomp). IR 3250, 2980, 1280, 1060, 1020 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.18 (s, 6H), 1.33 (s, 18H), 4.40 (s, 2H); ^{13}C NMR (100.6 MHz) δ −1.95 (s), 31.6 (s), 73.0 (s); ^{29}Si NMR (79.5 MHz) δ −53.1 (s). MS *m/z* 267 ($M^+ - 15$). Found: Si, 19.9%. Calcd for $C_{10}H_{24}O_5Si_2$: Si, 19.9%.

Synthesis of 1,1,3,3-Tetra-*t*-butoxydisiloxanediol (6). A mixture of THF (40 mL) and water (1.44 g, 0.08 mol) was added dropwise to a THF solution (100 mL) containing di-*t*-butoxydiisocyanatosilane (10.32 g, 0.04 mol) and triethylamine (0.40 g, 0.004 mol) at 0 °C. After reflux for 22 h, cyanuric acid was filtered. The filtrate was concentrated and hexane (50 mL) was added to precipitate cyanuric acid again. After filtration of cyanuric acid, 1,1,3,3-tetra-*t*-butoxy-1,3-diisocyanatodisiloxane **2** was isolated by distillation. (bp 110.5–111.3 °C/ 1.5 Torr, Yield 63.3%) (1 Torr≈ 133.322 Pa).

A THF solution (100 mL) containing water (0.72 g, 0.04 mol) and triethylamine (4.00 g, 0.04 mol) was added dropwise to a THF (10 mL) solution of **2** (8.96 g, 0.02 mol) at 0 °C. After reflux for 24 h, cyanuric acid was filtered. The filtrate was concentrated and hexane (50 mL) was added to precipitate cyanuric acid again. After filtration of cyanuric acid, the filtrate was concentrated and then dissolved to pentane to recrystallize **6**. Compound **6** was isolated as white plate crystals by the filtrering and drying under reduced pressure.

6 Yield: 56.7%. Mp 70.2–70.6 (decomp). IR 3400, 2980, 1070, 1010 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.35 (s, 36H), 3.91 (s, 2H); ^{13}C NMR (100.6 MHz) δ 31.3 (s), 73.4 (s); ^{29}Si NMR (79.5 MHz) δ −93.8 (s). MS *m/z* 383 ($M^+ - 15$). Found: Si, 14.1%. Calcd for $C_{16}H_{38}O_7Si_2$: Si, 14.0%.

Synthesis of 1,3-Di-*t*-butoxy-1,3-diisopropoxydisiloxanediol (7). A mixture of THF (80 mL), water (1.80 g, 0.10 mol) and triethylamine (2.04 g, 0.02 mol) was added dropwise to the THF solution (200 mL) containing *t*-butoxy(isopropoxy)diisocyanatosilane (48.8 g, 0.2 mol) at 0 °C. After reflux for 3 h, cyanuric acid was filtered. The filtrate was concentrated and hexane (100 mL) was added to precipitate cyanuric acid again. After filtration of cyanuric acid, 1,3-di-*t*-butoxy-1,3-diisopropoxy-1,3-diisocyanatodisiloxane **3** was isolated by distillation. (bp. 117–119 °C/ 2 Torr, yield 46.6%)

A mixture of THF (60 mL), water (3.60 g, 0.2 mol) and triethylamine (20.2 g, 0.2 mol) was added dropwise within 2 h to a THF solution (80 mL) containing **3** (42.0 g, 0.1 mol) at 0 °C. After filtration of cyanuric acid, the filtrate was concentrated and hexane (50 mL) was added to precipitate cyanuric acid again. After filtration of cyanuric acid, the filtrate was subjected to recrystallization, filtration and drying under reduced pressure to isolate **7** as a white powder.

7 Yield: 40.5%. Mp 74.0–77.6 (decomp). IR 3308, 2978, 1185, 1085, 967 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.22 (s, 12H), 1.35 (s, 18H), 4.30 (m, 2H), 4.61 (s, 1H); ^{13}C NMR (100.6 MHz) δ 25.3 (s), 31.3 (s), 66.0 (s), 73.4 (s); ^{29}Si NMR (79.5 MHz) δ −90.7 (s). MS *m/z* 355 ($M^+ - 15$). Found: Si, 14.4%. Calcd for $C_{16}H_{38}O_7Si_2$: Si, 14.3%.

Synthesis of Cyclic Metallasiloxanes (9–16). A solution of PTP (1.82 g, 0.005 mol) or PZP (2.04 g, 0.005 mol) in 10 mL of THF was added to a solution of **5**, **6**, **7**, or **8** (0.005 mol), followed by heating at 50 °C for 1 h. Solvents were removed under reduced pressures, followed by reprecipitation. The crude product was dissolved in 1 mL of THF and poured into 30 mL of hexane with vigorous stirring followed by filtration to give yellowish white powder.

2,4,8,10-Tetra-*t*-butoxy-2,4,8,10-tetramethyl-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dititana-1,3,5,7,9,11-hexaoxacyclododecane (9). Yield: 82.1%. Mp 162.4 (decomp). IR 2970, 1590, 1530, 1280, 1020, 1050, 990, 970 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.10 (s, 12H), 1.28 (s, 36H), 2.00 (s, 24H), 5.60 (s, 4H); ^{13}C NMR (100.6 MHz) δ −2.64 (s), 25.4 (s), 26.9 (s), 31.6 (s), 72.7 (s), 104.4 (s), 186.5 (s), 192.7 (s); ^{29}Si NMR (79.5 MHz) δ −55.7 (s). MS *m/z* 1052 (M$^+$). Found: Si, 10.5%. Calcd for $C_{40}H_{72}O_{18}Si_4Ti_2$: Si, 10.6%.

2,2,4,4,8,8,10,10-Octa-*t*-butoxy-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dititana-1,3,5,7,9,11-hexaoxacyclododecane (10). Yield: 81.9%. Mp 126.3 (decomp). IR 2970, 1580, 1530, 1070, 1020, 960 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.31 (s, 72H), 1.99 (s, 24H), 5.63 (s, 4H); ^{13}C NMR (100.6 MHz) δ 25.4 (s), 26.8 (s), 31.3 (s), 72.5 (s), 104.3 (s), 187.6 (s), 192.3 (s); ^{29}Si NMR (79.5 MHz) δ −96.6 (s). MS *m/z* 1211 (M$^+$−73). Found: Si, 8.5%. Calcd for $C_{52}H_{100}O_{22}Si_4Ti_2$: Si, 8.5%.

2,4,8,10-Tetra-*t*-butoxy-2,4,8,10-tetraisopropoxy-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dititana-1,3,5,7,9,11-hexaoxacyclododecane (11). Yield: 72.3%. Mp 167.0–169.8 (decomp). IR 2977, 1708, 1592, 1106, 1070, 970 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.22 (s, 24H), 1.34 (s, 36H), 1.99 (s, 24H), 4.29 (s, 4H) 5.99 (s, 4H); ^{13}C NMR (100.6 MHz) δ 23.9 (s), 25.4 (s), 26.8 (s), 31.6 (s), 65.9 (s), 74.6 (s), 104.7 (s), 187.9 (s), 192.6 (s); ^{29}Si NMR (79.5 MHz) δ −92.5 (s). VPO M_n 1290. Found: Si, 9.2%. Calcd. for $C_{48}H_{92}O_{22}Si_4Ti_2$: Si, 9.2%.

2,2,4,4,8,8,10,10-Octaphenyl-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dititana-1,3,5,7,9,11-hexaoxacyclododecane (12). Yield: 85.2%. Mp 197.9 (decomp). IR 3060, 2970, 1580, 1530, 1130, 1015, 940 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.84 (br, 24H), 5.61 (s, 4H), 7.25 (m, 40H); ^{13}C NMR (100.6 MHz) δ 24.9 (s), 25.8 (s), 103.9 (d), 134.9 (q), 186.8 (s), 191.4 (s); ^{29}Si NMR (79.5 MHz) δ −37.9 (s). MS *m/z* 1273 (M$^+$−43). Found: Si, 8.4%. Calcd for $C_{68}H_{68}O_{14}Si_4Ti_2$: Si, 8.5%.

2,4,8,10-Tetra-*t*-butoxy-2,4,8,10-tetramethyl-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dizircona-1,3,5,7,9,11-hexaoxacyclododecane (13). Yield: 78.1%. Mp 159.5 (decomp). IR 2970, 1590, 1530, 1280, 1010, 1040, 990, 950 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.09 (s, 12H), 1.29 (s, 36H), 1.96 (s, 24H), 5.61 (s, 4H); ^{13}C NMR (100.6 MHz) δ −2.64 (s), 26.9 (s), 31.5 (s), 72.7 (s), 104.4 (s), 190.9 (s); ^{29}Si NMR (79.5 MHz) δ −64.9 (s). MS *m/z* 1123 (M$^+$−15). Found: Si, 9.8%. Calcd for $C_{40}H_{72}O_{18}Si_4Zr_2$: Si, 9.8%.

2,2,4,4,8,8,10,10-Octa-*t*-butoxy-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dizircona-1,3,5,7,9,11-hexaoxacyclododecane (14). Yield: 85.5%. Mp 132.5 (decomp). IR 2970, 1600, 1530, 1070, 1020, 920 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.32 (s, 72H), 1.99 (s, 24H), 5.50 (s, 4H); ^{13}C NMR (100.6 MHz) δ 26.7 (s), 31.5 (s), 71.5 (s), 102.9 (s), 189.6 (s); ^{29}Si NMR (79.5 MHz) δ −102.8 (s). MS *m/z* 1297 (M$^+$−73). Found: Si, 8.1%. Calcd for $C_{52}H_{100}O_{22}Si_4Zr_2$: Si, 8.1%.

2,4,8,10-Tetra-*t*-butoxy-2,4,8,10-tetraisopropoxy-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dizircona-1,3,5,7,9,11-hexaoxacyclododecane (15). Yield: 70.5%. Mp 178.3–180.0 (decomp). IR 2981, 1710, 1592, 1105, 970, 916 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.21 (s, 24H), 1.34 (s, 36H), 1.97 (s, 24H), 4.31 (s, 4H) 5.98 (s, 1H); ^{13}C NMR (100.6 MHz) δ 25.6 (s), 26.6 (s), 31.6 (s), 65.8 (s), 73.9 (s), 104.4 (s), 190.2 (s); ^{29}Si NMR (79.5 MHz) δ −101.0 (s). VPO M_n 1385. Found: Si, 8.4%. Calcd for $C_{48}H_{92}O_{22}Si_4Zr_2$: Si, 8.5%.

2,2,4,4,8,8,10,10-Octaphenyl-6,6,12,12-tetrakis(2,4-pentanedionato-κ^2O)-2,4,8,10-tetrasila-6,12-dizircona-1,3,5,7,9,11-hexaoxacyclododecane (16). Yield: 96.1%. Mp 211.7 (decomp). IR 3060, 2970, 1580, 1530, 1120, 1015, 930 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.92–1.86 (m, 24H), 5.63 (t, 4H), 7.23 (m, 40H); ^{13}C NMR (100.6 MHz) δ 26.3 (s), 26.7 (s), 103.0 (d), 134.6 (q), 189.7 (s), 191.1 (s); ^{29}Si NMR (79.5 MHz) δ −47.6 (s), −49.4 (s). MS *m/z* 1402 (M$^+$). Found: Si, 7.9%. Calcd for $C_{68}H_{68}O_{14}Si_4Zr_2$: Si, 8.0%.

Pyrolysis of Cyclic Metallasiloxanes. Cyclic metallasiloxane **9**–**16** was placed on an alumina plate and then subjected to pyrolysis under air atmosphere by raising the temperature at the rate of 2 °C/min. When the temperature reached to the target temperature, the temperature was held for 1 h and then cooled to room temperature. The resulting product was subjected to IR measurements and X-ray analysis.

Measurements and Analyses. ^{1}H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) spectra were acquired using a JOEL JNM-EX-400 spectrometer in chloroform-*d*. Fourier-transformed infrared (FT-IR) spectra were measured using a JEOL FT-IR-400 IR spectrophotometer by means of carbon tetrachloride solution method or KBr disk method. The mass (MS) spectra were obtained using Shimadzu GCMS-QP2000A equipped with a direct insertion apparatus. Thermogravimetry was performed using a RIGAKU thermoflex TAS-100 under air atmosphere. X-ray diffraction was analyzed by using a RIGAKU CN-2013.

The metal content was determined by following procedure. At first, 0.2 g of sample was weighed in a crucible and sulfuric acid (0.5 mL) was added. After gradual heating of the Kjeldahl flask overnight, the residue was weighed (A). Second, 0.2 g of sample was weighed in a flask and heated in the presence of ammonium sulfate (1 g), ammonium nitrate (1 g), and sulfuric acid (20 mL). The residue was poured into 100 g of ice, followed by filtration. The filtrate was subjected to firing in a crucible, followed by weighing (B). The content of SiO_2 was calculated from the content (B) and the content of TiO_2 or ZrO_2 was calculated from the difference between the contents (A) and (B).

Conclusion

Disiloxane-1,3-diols $[(HO)SiR^1R^2]_2O$ ($R^1 = Me, R^2 = OBu^t$; $R^1 = R^2 = OBu^t$; $R^1 = OPr^i, R^2 = OBu^t$) were synthesized by the hydrolysis of corresponding 1,3-diisocyanatodisiloxanes. The reaction of disiloxane-1,3-diols with diisopropoxidobis(2,4-pentanedionato)titanium or diisopropoxidobis(2,4-pentanedionato)zirconium in tetrahydrofuran provided cyclic metallasiloxanes, $[(SiR^1R^2O)_2M(acac)_2O]_2$ ($R^1 = Me, R^2 = OBu^t$; $R^1 = R^2 = OBu^t$; $R^1 = OPr^i, R^2 = OBu^t$; M = Ti, Zr). These compounds consisted of twelve-membered rings, (Si–O–Si–O–Ti–O)$_2$ or (Si–O–Si–O–Zr–O)$_2$.

The pyrolysis of cyclic titanasiloxanes and zirconasiloxanes provided $2SiO_2$–TiO_2 and $2SiO_2$–ZrO_2 ceramics, respectively. On the pyrolysis of cyclic titanasiloxanes, titanium component in the molecule crystallized in titania anatase form. The crystallization temperature was independent of the side chain groups on silicon atom. Zirconium component also crystallized to tetragonal form on the pyrolysis of cyclic zirconasiloxanes.

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