The Thermal Changes in Gels of the SiO_2–Al_2O_3–In_2O_3–H_2O System

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The synthesized coprecipitated gels in the SiO_2–Al_2O_3–In_2O_3–H_2O system showed an allophane-like pattern in the DTA except for the indium-rich gels. The exothermic peak temperature in the DTA was lowered from 980 to 940 °C with an increase in the indium content, while that on mixed gels was scarcely lowered at all. A new small exothermic peak around 880 °C in the DTA was observed in the coprecipitated gels with more than 11.93 wt% of In_2O_3; it was considered to be due to the structural change in the gels which arose from the formation of the indium (III) oxide. The firing products of the coprecipitated gels were identified as mullite, indium (III) oxide, and indium (III) silicate. The mullite formed in the coprecipitated gels included indium ions at 900 °C, accompanied by an increase in its unit cell volume, while the indium ions were almost entirely removed from the mullite lattice at 1200 °C.

The thermal properties of coprecipitated gels, the SiO_2–Al_2O_3–Fe_2O_3–H_2O[1] and the SiO_2–Al_2O_3–Ga_2O_3–H_2O[2] systems, have been studied. It has been found that aluminum ions are replaced by iron (III) or gallium ions in the allophane structure of the coprecipitated gels. The thermal properties of the gels in the SiO_2–Al_2O_3–In_2O_3–H_2O system have not been studied, while phase diagrams of the In_2O_3–Al_2O_3[3] and the In_2O_3–Ga_2O_3[4] systems have been reported.

In this work, the thermal properties of the coprecipitated gels in the SiO_2–Al_2O_3–In_2O_3–H_2O system were studied in order to determine the role of trivalent cations in a silicoalumina-gel structure.

Experimental

Materials. The samples were prepared by means of a method similar to that described in previous papers:[1,2] indium-coprecipitated gels were obtained by boiling mixed solutions of aluminum sulfate, indium(III) sulfate, and sodium silicate at a pH of about 4.5, a pH value obtained by adding hexamethylenetetramine. The $In_2O_3/(Al_2O_3+In_2O_3)$ molar ratio in the mixed solutions was varied from zero to 1.0 at a constant molar ratio of 2.0 as $SiO_2/(Al_2O_3+In_2O_3)$. The gels thus coprecipitated were washed by decantation and then air-dried for three weeks. They were identified as amorphous from their X-ray powder diffractograms. The indium-mixed gels were prepared by mixing a synthesized allophane, free from indium, and an amorphous hydrated indium(III) oxide in order to compare the properties of the coprecipitated gels. The hydrated indium(III) oxide was prepared by using ammonia water at pH 4.0. The gel thus obtained was identified as amorphous from its X-ray powder diffractogram, though the gels obtained at pH 5.3 and 7.0 contained crystalline InOOH.[5-7]

Procedure. The contents of SiO_2, Al_2O_3, and $H_2O(\pm)$[8] in the samples were estimated gravimetrically, and that of In_2O_3,[9] polarographically.

The differential thermal analysis for the sample was carried out at the heating rate of 10 °C/min in the temperature range from room temperature to 1000 °C with a Rigaku Denki Thermoflex, model 8002, differential thermal analyzer.

The X-ray powder diffractogram of the sample was taken by using an X-ray diffractometer, model JDX-5P, from the Japan Electron Optics Laboratory Co. The sample, in a quartz tube, was heated at 800, 900, 1000, 1100, and 1200 °C for 5 hr, and at 1300 °C for 1 hr, in an electric furnace. The firing products were identified, and their relative amounts were estimated by using the diffraction peaks at (120) and (210) of the mullite, that at (101) of the cristobalite, and those at (222) and (400) of the indium (III) oxide. The unit-cell dimensions of the mullite and the indium (III) oxide, the firing products of the samples, were calculated by using the peaks at (121), (230), (400), (041), (331), and (002) of the mullite and those at (222), (400), and (440) of the indium (III) oxide. The diffraction angles were calibrated with those of silicon.

Results and Discussion

The chemical compositions of the indium-bearing gels are shown in Table 1. The molar ratios of $SiO_2/(Al_2O_3+In_2O_3)$ in the coprecipitated gels were smaller than those of $SiO_2/(Al_2O_3+Ga_2O_3)$ in the gallium-coprecipitated gels[2] obtained from the mixed solutions with the same molar ratio of 2.0, except for the In-12C sample. These small values of the molar ratios were considered to arise from the condition of a higher acidity for precipitation than that for the gallium-coprecipitated gels, or from the nature of the indium (III) ion.

The Differential Thermal Analysis of the Samples. The DTA patterns of the gels are shown in Fig. 1. The In-0 sample, free from indium, was identified as an allophane from its DTA pattern, attributable to allophane. The exothermic peak temperature was lowered from 980 to 940 °C as the indium content increased, except for the In-8C and -9C samples, in contrast to the small shift in the mixed gels. This peak was not observed in the gels with more than 38.22 wt% of In_2O_3 (the In-10C and -11C samples). The tendency of the peak temperature in the indium-coprecipitated gels to lower was considerably less than that in the gallium-coprecipitated gels.[2]

The apparent activation energy, E_a, for the exothermic change around 980 °C was estimated by means of the Kissinger equation.[10] The E_a values of the exothermic change in the coprecipitated gels decreased with an increase in the indium content, while those in the mixed gels were nearly equal to that in the In-0 sample, as is shown in Table 2.

A new, small, broad exothermic peak around 880 °C in the DTA was observed in only the coprecipitated gels with more than 11.93 wt% of In_2O_3 (from the In-3C to -12C samples); the mixed gels did not show it.

TABLE 1. CHEMICAL COMPOSITIONS OF INDIUM-BEARING SAMPLES

Samples	Chemical composition, wt%					Molar ratio	
	SiO_2	Al_2O_3	In_2O_3	H_2O (±)	Total	$\frac{SiO_2}{R_2O_3}$ [a]	$\frac{H_2O\ (\pm)}{R_2O_3}$ [a]
In-0 [b]	25.75	29.73	0	45.28	100.76	1.47	8.63
In-1C [c]	25.30	28.41	3.82	42.88	100.41	1.44	8.14
In-2C	22.63	29.04	6.93	41.84	100.44	1.22	7.47
In-3C	23.09	23.77	11.93	40.84	99.63	1.38	8.18
In-4C	23.11	22.52	15.67	39.20	100.50	1.38	8.20
In-5C	21.89	21.44	19.46	37.61	100.40	1.29	7.38
In-6C	22.52	19.63	22.56	35.40	100.11	1.35	7.11
In-7C	19.61	20.36	24.93	34.63	99.53	1.11	6.57
In-8C	21.23	18.25	27.53	32.49	99.50	1.25	6.41
In-9C	21.03	14.13	34.03	30.38	99.57	1.32	6.35
In-10C	20.96	13.41	38.22	26.84	99.43	1.27	5.44
In-11C	16.82	6.91	50.85	24.91	99.49	1.09	4.41
In-12C	26.14	0	50.45	23.99	100.58	2.31	7.07
In-13M [c]	24.79	28.62	1.64	44.95	100.00 [d]	1.44	8.71
In-14M	24.18	27.92	3.29	44.62	100.00 [d]	1.41	8.67
In-15M	23.31	26.92	5.62	44.15	100.00 [d]	1.36	8.61
In-16M	22.30	25.75	8.34	43.61	100.00 [d]	1.31	8.54
In-17M	19.00	21.95	17.24	41.82	100.00 [d]	1.13	8.31
In-18M	16.10	18.60	25.04	40.26	100.00 [d]	0.97	8.10
In-19M	32.70	0	8.00	59.30	100.00 [d]	4.09	7.41

a) $Al_2O_3+In_2O_3$. b) Allophane, free from indium. c) The postscripts "C" and "M" denote the coprecipitated and the mixed samples, respectively. d) Calculated.

TABLE 2. APPARENT ACTIVATION ENERGY FOR EXOTHERMIC CHANGE AROUND 980 °C

Sample	E_a, kcal/mol
In-0	250
In-1C	237
In-5C	196
In-14M	245

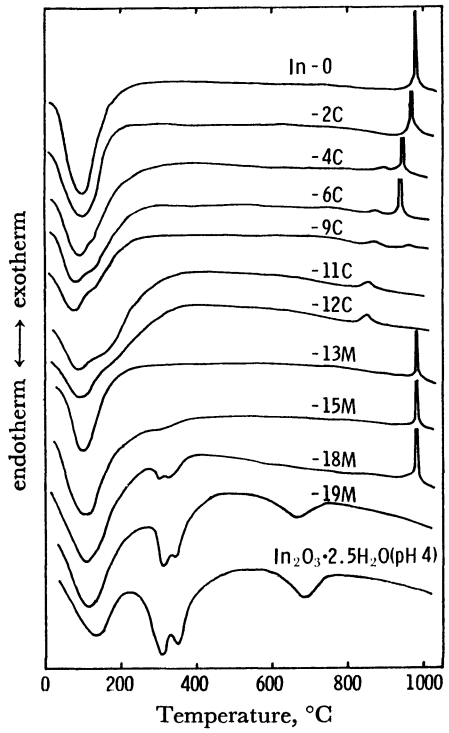

Fig. 1. DTA curves of indium-bearing samples.

This exothermic peak temperature was also lowered continuously with an increase in the indium content.

In the indium-rich mixed gels, the endothermic peaks based on the amorphous hydrated indium (III) oxide were observed besides the endo- and the exothermic peaks around 100 and 980 °C.

The Variation in the Firing Products in the Samples during the Heat Treatment. The crystalline phases formed

TABLE 3. FIRING PRODUCTS IN INDIUM-BEARING SAMPLES

Sample	Temperature, °C					
	800	900	1000	1100	1200	1300
In-0	A	M	M	M	M	M
In-1C	A	M	M	M, I	M, I, C, IS	
In-2C	A	M, I	M, I	M, I	M, I, IS	M, IS
In-3C	A	M, I	M, I	M, I	M, I, IS	M, IS
In-4C	A	M, I	M, I	M, I	M, I, IS	
In-5C	A	M, I	M, I	M, I	M, I, IS	
In-6C	I	M, I	M, I	M, I	M, I, IS	M, IS
In-7C	I	M, I	M, I	M, I, IS	M, I, IS	
In-8C	I	M, I	M, I	M, I, IS	M, I, IS	
In-9C	I	I	I	M, I, IS	M, I, IS	
In-10C	I	I	I	M, I, IS	M, I, IS	M, IS
In-11C	I	I	I	I, IS	I, IS	
In-12C	I	I	I	I	I	I
In-13M	I	M, I	M, I	M, I	M, I, IS	
In-14M	I	M, I	M, I	M, I	M, I, IS	
In-15M	I	M, I	M, I	M, I	M, I, IS	
In-16M	I	M, I	M, I	M, I	M, I, IS	
In-17M	I	M, I	M, I	M, I	M, I	
In-18M	I	M, I	M, I	M, I	M, I	
In-19M	I	I	I	I	I	

A: amorphous, M: mullite, I: indium (III) oxide, IS: indium (III) silicate (new phase), C: cristobalite.

in the samples heat-treated at 800, 900, 1000, 1100, and 1200 °C for 5 hr, and at 1300 °C for 1 hr were identified by X-ray powder diffractometry as mullite, indium (III) oxide, and a new phase, as Table 3 shows.

The indium (III) oxide formed below 1000 °C in the coprecipitated gels with more than 11.93 wt% of In_2O_3 (from the In-3C to -11C samples) showed broad X-ray powder diffraction peaks; their spacings were smaller than those of the indium (III) oxide with the usual unit-cell dimensions.[11] This contraction of the crystal lattice was considered to arise from the replacement with aluminum ions.

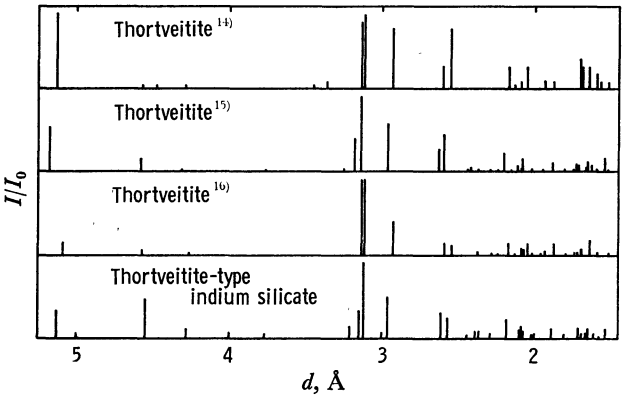

Fig. 2. X-ray powder diffraction patterns of thortveitite and thortveitite-type indium silicate.

New X-ray diffraction peaks were observed in the firing products above 1100 or 1200 °C of the indium-bearing gels, except for those of the In-17M and -18M samples, and the aluminum-free samples. This X-ray diffraction pattern, without the diffraction peaks of the known materials, was found to resemble closely that of thortveitite, $Sc_2Si_2O_7$, as is shown in Fig. 2. In the coprecipitated gels of the SiO_2–Al_2O_3–Sc_2O_3–H_2O system, a large portion of their scandium component was confirmed to separate out as thortveitite upon heating.[12] In this system, cristobalite was not found as a firing product, except in the In-1C sample, just as in the system of SiO_2–Al_2O_3–Sc_2O_3–H_2O. In the iron (III)- and the gallium-bearing systems,[1,2] excess amounts of such trivalent cations as iron (III) and gallium ions separated out as hematite and β-gallia with the formation of cristobalite at higher temperatures. Judging from the above facts and a similarity in their ionic radii (In^{3+}: 0.81 and Sc^{3+}: 0.73 Å[13]), the new phase was considered to be a thortveitite-type indium (III) silicate; it has not been found in nature, but only as a synthesized mineral. It is assumed that the crystal structure of the new phase is the same as that of thortveitite (monoclinic); the unit-cell dimensions were calculated by means of the least-squares method, using all the observed spacings (27 spacings up to 1.58 Å), as is shown in Table 4. The spacings and their Miller indices of the indium (III) silicate are shown in Table 5. It can be concluded from the results presented in Tables 4 and 5 that the new phase found in this work is thortveitite-type indium (III) silicate; however, it could not be identified chemically because it could not be isolated. The SiO_2/In_2O_3 molar ratio in the indium-rich mixed gels and the aluminum-free gels in this system were considered not to be effective in the formation of indium (III) silicate upon heating.

Table 4. Unit-cell dimensions of thortveitite and thortveitite-type indium silicate

Specimen	a_0, Å	b_0, Å	c_0, Å	β, °	Remarks
Thortveitite	6.57	8.60	4.57	103.1	Native[14]
Thortveitite	6.65	8.62	4.68	102.2	Native[15]
Thortveitite	6.508	8.506	4.677	102.72	Synthesized[16]
Indium silicate	6.58	8.58	4.70	102.9	This work

Table 5. Spacings and their Miller indices of indium silicate

h k l	d, Å Calcd	d, Å Obsd	I/I_0	h k l	d, Å Calcd	d, Å Obsd	I/I_0
1 1 0	5.14	5.13	38	$\bar{2}$ 0 2	2.10	2.10	12
0 0 1	4.58	4.55	53	2 2 1	2.09	2.09	16
0 2 0	4.29	4.28	14	3 1 0	2.07	2.07	11
$\bar{1}$ 1 1	3.77	3.77	7	0 2 2	2.02	2.02	6
2 0 0	3.21	3.21	16	$\bar{2}$ 2 2	1.89	1.89	14
1 1 1	3.15	3.15	37	$\bar{1}$ 3 2	1.81	1.81	6
0 2 1	3.13	3.12	100	3 3 0	1.71	1.71	14
$\bar{2}$ 0 1	2.96	2.96	55	2 0 2	1.69	1.69	7
1 3 0	2.61	2.61	34	1 5 0	1.66	1.66	8
2 2 0	2.57	2.57	27	1 3 2	1.65	1.65	13
$\bar{2}$ 2 1	2.43	2.44	6	4 0 0	1.60	1.61	6
2 0 1	2.39	2.39	11	2 2 2	1.57	1.58	3
$\bar{1}$ 3 1	2.36	2.36	11	1 5 1 }	1.53	1.53	13
0 0 2	2.29	2.28	7	0 0 3 }			
1 3 1	2.19	2.18	26				

The cause of the exothermic peaks around 980 and 880 °C in the DTA was examined as follows: the In-0, -1C, -9C, -12C, and -15M samples were preheated in the DTA equipment up to temperatures just below and above their peak temperatures. The phases of the preheated samples were found by X-ray powder diffractometry to be as are shown in Table 6. While the exothermic changes around 980 and 880 °C were found to be related to the formations of the mullite and the indium (III) oxide, it could not be confirmed whether or not both the exothermic peaks themselves depended on the formations of the mullite and the indium (III) oxide. They might be caused by the same structural changes[2] in the coprecipitated gels which brought about the formations of the mullite and the indium (III) oxide.

Table 6. Phases of preheated samples

Sample	Peak temp. of original state, °C	Phases after heat treatment: below peak temp.	Phases after heat treatment: above peak temp.
In-0	980	A (950 °C)	M (990 °C)
In-1C	965	A (945 °C)	M (975 °C)
In-9C	866	A (852 °C)	I (876 °C)
In-12C	852	A (830 °C)	I (860 °C)
In-15M	980	I (950 °C)	I, M (990 °C)

A: amorphous, M: mullite, I: indium (III) oxide.

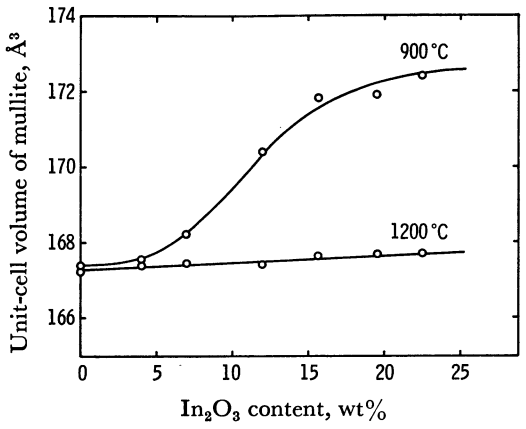

Fig. 3. Plot of unit-cell volume of mullite formed in coprecipitated gels against indium content.

The Unit-cell Volume of the Mullite Formed in the Heat-treated Samples. The unit-cell volumes of the mullite formed in the coprecipitated gels at 900 and 1200 °C for 5 hr were estimated to be as are shown in Fig. 3; those in the gels with more than 25 wt% of In_2O_3 could not be estimated because of the weak intensity of their diffraction peaks. The unit-cell volume of the mullite formed at 900 °C increased with the increase in the indium content when the indium (III) ions were included, while those in the mixed gels scarcely changed at all.

On the contrary, the unit-cell volume of the mullite decreased at 1200 °C as the crystallization proceeded with the removal of the indium (III) ions; then it became nearly equal to that in the indium-free coprecipitated gels. The exclusion of the indium (III) ions at 1200 °C from the mullite lattice was considered to arise from its large ionic radius, though the gallium ions were included in the mullite in fairly large quantities, even at 1200 °C.[2)]

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