The Thermal Properties of Gallium-bearing Allophane

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(Received February 8, 1973)

The DTA patterns of synthesized coprecipitated gels, SiO_2–Al_2O_3–Ga_2O_3–H_2O system, resembled that of allophane, and the exothermic peak temperature in the DTA was lowered continuously from 980 to 810 °C with an increase in the gallium content, while that on mixed gels scarcely lowered. The apparent activation energy for this exothermic reaction on the coprecipitated gels decreased with an increase in the gallium content, while that on the mixed gels hardly changed. The crystallization process during the heat treatment of the gels depended on the content and on the coexistence state of the gallium. A unit cell volume of a mullite crystallized at 1200 °C in the coprecipitated gels was enlarged by forming a solid solution with the gallium ion, in contrast to the small change in that formed in the mixed gels. Further, the exothermic peak in the DTA was considered to originate not only from the formation of the mullite, but also from that of the silico-alumina spinel in the gallium-bearing gels; the exothermic reaction products seem to depend on the composition or the coexistence state of gallium in the gels.

The lower crystalline minerals of the SiO_2–Al_2O_3–H_2O system, found in nature as allophane, frequently contain iron. In a previous paper,[1] a synthesized iron-coprecipitated gel was recognized to be an iron-bearing allophane. Gallium occurs widely, but in trace amounts, and it is considered to coexist as a solid solution in aluminum minerals, as in nature. Mixed systems of aluminum and gallium have been studied in connection with those of the Al_2O_3–Ga_2O_3–H_2O system,[2] $(Al, Ga)_2O_3$,[3,4] $2SiO_2\cdot 3(Al, Ga)_2O_3$,[5] and gallium-bearing feldspar.[6]

In this work, the properties of the synthesized gallium-coprecipitated gels of the SiO_2–Al_2O_3–Ga_2O_3–H_2O system were studied in order to examine the coexistence state of gallium in them.

Experimental

Materials. The gallium-coprecipitated samples were prepared in the following manner:[1,7] coprecipitated gels were obtained by boiling mixed solutions of aluminum sulfate, sodium silicate, and gallium sulfate at pH 5.9—6.4, a pH value obtained by adding hexamethylenetetramine. The $Ga_2O_3/(Al_2O_3+Ga_2O_3)$ molar ratio in the mixed solutions was varied from zero to 1.0 at a constant molar ratio of 2.0 as $SiO_2/(Al_2O_3+Ga_2O_3)$. The gels thus coprecipitated were washed by decantation and then air-dried for three weeks. The gallium-mixed samples were prepared by mixing a synthesized allophane, free from gallium, and a hydrated gallium(III) oxide in order to compare the properties of the coprecipitated samples. The amorphous hydrated gallium(III) oxide was prepared by precipitation with ammonia water at pH 4.0 and by subsequent air-drying, like the coprecipitated samples, as one of the components in the mixed samples. The air-dried hydrated gallium(III) oxide gel obtained at pH 4.0 was identified as amorphous from its X-ray powder diffraction pattern, and its chemical composition was estimated to be $Ga_2O_3\cdot 4.1H_2O$ (corresponding to $Ga(OH)_3\cdot 0.5H_2O$) from the ignition loss, though the air-dried gels obtained at pH 5.3 and 7.7 were found to contain a crystalline GaOOH[8] and their chemical compositions were $Ga_2O_3\cdot 2.0H_2O$ and $Ga_2O_3\cdot 1.2H_2O$ (corresponding to $Ga(OH)_3\cdot GaOOH$ and $Ga(OH)_3\cdot 9GaOOH$) respectively.

Procedure. The chemical compositions of the samples were estimated gravimetrically for SiO_2, Al_2O_3, and $H_2O(\pm)$,[9] and colorimetrically for Ga_2O_3.[10]

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

The X-ray powder diffractogram of the sample was taken with an X-ray diffractometer, model JDX-5P, of the Japan Electron Optics Laboratory Co. The diffraction angles were calibrated by using those of silicon. The sample, in a quartz tube, was heated at 800, 900, 1000, 1100, and 1200 °C for 5 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, those at (200) and (004) of the β-gallia, and those at (220) and (311) of the silico-alumina spinel. The unit-cell dimensions of the mullite, one of the firing products at 1200 °C, were calculated by using the diffraction peaks at (400), (041), (331), and (002) of the mullite.

Results

The chemical compositions of the gallium-bearing samples are shown in Table 1. The $SiO_2/(Al_2O_3+Ga_2O_3)$ and the $H_2O(\pm)/(Al_2O_3+Ga_2O_3)$ molar ratios in the coprecipitated samples decreased with an increase in the gallium content, while the $H_2O(\pm)/(Al_2O_3+Ga_2O_3)$ ratio in the mixed samples did not vary in spite of the change in the gallium content.

The Differential Thermal Analysis of the Samples. All the samples were amorphous or lower crystalline materials, for there were few sharp X-ray powder diffraction peaks. The Ga-0 sample, free from gallium, showed a broad endothermic peak and a sharp exothermic peak at 100 and 980 °C respectively in the

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[1] J. Ossaka, S. Iwai, M. Kasai, T. Shirai, and S. Hamada, This Bulletin, **44**, 716 (1971).

[2] V. G. Hill, R. Roy, and E. F. Osborn, *J. Amer. Ceram. Soc.*, **35**, 135 (1952).

[3] J. McDonald, J. A. Gard, and F. P. Glasser, *J. Inorg. Nucl. Chem.*, **29**, 661 (1967).

[4] J. A. Gard, *Bull. Groupe France Argiles*, **17**, 19 (1966).

[5] G. Gelsdorf, H. Hüller-hesse, and H. E. Schwiete, *Arch. Eisenhüttenw.*, **29**, 513 (1958).

[6] J. R. Goldsmith, *J. Geol.*, **58**, 518 (1950).

[7] J. Ossaka, S. Iwai, M. Kasai, T. Shirai, and S. Hamada, *Nippon Kagaku Zasshi*, **90**, 1288 (1969).

[8] R. Roy, V. G. Hill, and E. F. Osborn, *J. Amer. Chem. Soc.*, **74**, 719 (1952).

[9] The values were estimated from the ignition loss.

[10] T. Moeller, *Anal. Chem.*, **22**, 686 (1950).

TABLE 1. CHEMICAL COMPOSITIONS OF GALLIUM-BEARING SAMPLES

Sample	Chemical composition, wt%					Molar ratio	
	SiO_2	Al_2O_3	Ga_2O_3	$H_2O(\pm)$	Total	SiO_2/R_2O_3[a]	$H_2O(\pm)/R_2O_3$[a]
Ga-0[b]	36.34	29.66	0	33.86	99.86	2.07	6.46
Ga-1C[c]	37.16	31.04	1.13	30.98	100.31	1.99	5.54
Ga-2C	37.32	27.59	2.82	31.76	99.39	2.13	6.00
Ga-3C	35.62	28.03	4.64	32.43	100.72	1.98	6.00
Ga-4C	36.56	27.18	5.67	30.93	100.34	2.05	5.79
Ga-5C	36.47	27.22	6.39	29.74	99.82	2.02	5.49
Ga-6C	36.45	25.76	7.84	29.51	99.61	2.06	5.57
Ga-7C	36.18	24.57	10.52	28.98	100.25	2.02	5.42
Ga-8C	35.36	22.65	15.25	27.36	100.62	1.94	5.01
Ga-9C	33.66	20.64	17.72	28.44	100.46	1.89	5.32
Ga-10C	33.07	19.61	19.64	27.72	100.04	1.85	5.18
Ga-11C	32.76	17.34	23.53	26.74	100.37	1.84	5.03
Ga-12C	32.29	16.71	25.83	25.68	100.52	1.78	4.73
Ga-13C	30.50	11.70	34.57	23.53	100.30	1.70	4.37
Ga-14C	26.48	0	53.01	20.65	100.14	1.56	4.06
Ga-15M[c]	34.68	28.30	2.82	34.07	99.87	1.97	6.46
Ga-16M	32.47	26.50	6.57	34.46	100.00[d]	1.83	6.49
Ga-17M	30.25	24.69	10.32	34.74	100.00[d]	1.69	6.49
Ga-18M	27.40	22.36	15.16	34.98	99.90	1.52	6.47
Ga-19M	22.45	18.33	23.54	35.60	99.92	1.22	6.48

a) $Al_2O_3+Ga_2O_3$. b) Allophane, free from gallium. c) The postscripts " C " and " M " denote the coprecipitated and mixed samples, respectively. d) Calculated.

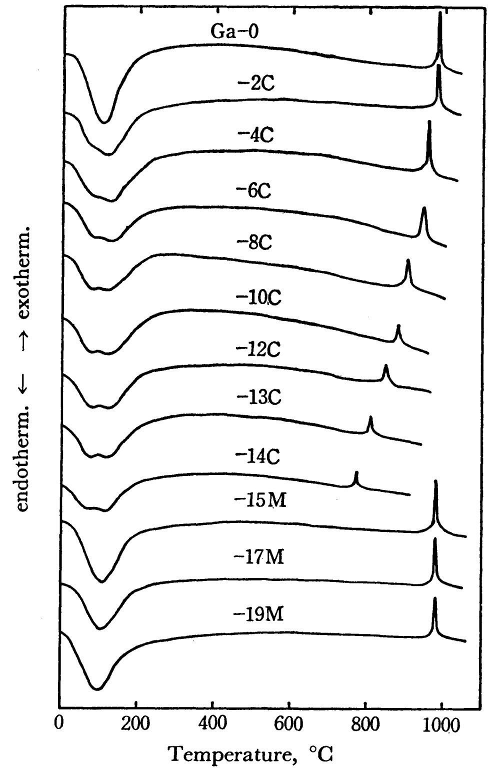

Fig. 1. DTA curves of gallium-bearing samples.

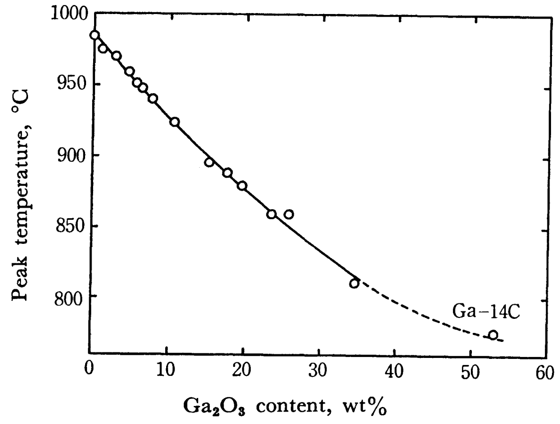

Fig. 2. Plot of exothermic-peak temperature in DTA of coprecipitated samples against gallium content.

DTA which were assigned to the allophane. The patterns of the DTA of the samples were also similar to that of the allophane, though the endothermic peak split into two peaks with an increase in the gallium content, as is shown in Fig. 1. The exothermic peak temperature in the DTA on the coprecipitated samples was lowered from 980 to 810 °C with an increase in the gallium content, in contrast to the small shift of the exothermic peak temperature of the mixed samples, as is shown in Fig. 2. The peak temperature of the Ga-14C sample, free from aluminum, was 775 °C.

The Variation in the Firing Products in the Samples during Heat Treatment. The crystalline phases formed in the heat-treated samples at 800, 900, 1000, 1100, and 1200 °C for 5 hr were identified as the mullite, the silico-alumina spinel,[11] the β-gallia, and the cristobalite by means of X-ray powder diffractometry. The firing products at each temperature are shown in Table 2. The crystallization process of the coprecipitated samples was found to vary, depending on the con-

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[11] G. W. Brindley and M. Nakahira, *J. Amer. Ceram. Soc.*, **42**, 314 (1959).

Table 2. Firing products in gallium-bearing samples

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

A: amorphous, M: mullite, Sp: silico-alumina spinel, G: β-gallia, C: cristobalite.

dition of the original samples, as is shown in Table 2. The crystallization of the mullite tended to become difficult with an increase in the gallium content of the samples; thus, the mullite was not observed as a firing product in the samples with more than 25.83 wt% of Ga_2O_3.

On the contrary, the crystallization process of the mixed samples was analogous with each other in spite of the variation in the gallium content without forming the silico-alumina spinel. Therefore, the coexistence state of gallium in the coprecipitated samples were considered to be different from that of the mixed samples, judging from the dissimilarity between the crystallization processes of the coprecipitated and of the mixed samples.

In order to examine the cause of the exothermic peak around 900 °C in the DTA, the Ga–1C, -3C, -8C, -11C, -13C, -14C, and -16M samples were preheated up to temperatures just below and above their peak temperatures at the rate of 10 °C/min in the DTA equipment. The phases of these preheated samples were identified by X-ray diffractometry to be as is shown in Table 3. When these samples were again examined by the DTA, the sharp exothermic peak was observed only in the samples which retained the amorphous state after preheating just below the peak temperatures, except for the Ga–16M sample. As is shown in Table 3, the exothermic change in the coprecipitated samples was found to lead to the formation of the mullite or the silico-alumina spinel from the amorphous state.

The apparent activation energy, E_a, for the exothermic change was estimated by the following Kissinger equation:[12]

$$d(\ln \theta/T_m^2)/d(1/T_m) = -E_a/R$$

where θ is the heating rate (3, 5, 10, 15, and 20 °C/min); T_m, the peak temperature in the DTA, and R, the gas constant.

Table 3. Phases of preheated samples

Sample	Peak temp. of original state, °C	Phase after heat treatment	
		below peak temp.	above peak temp.
Ga-1C	975	A (960 °C)	M (990 °C)
Ga-3C	959	A (930 °C)	M (985 °C)
Ga-8C	895	A (872 °C)	Sp (910 °C)
Ga-11C	859	A (848 °C)	Sp (875 °C)
Ga-13C	810	A (798 °C)	Sp (834 °C)
Ga-14C	775	A (762 °C)	Sp (787 °C)
Ga-16M	980	G (970 °C)	M, G (995 °C)

A: amorphous, M: mullite, Sp: silico-alumina spinel, G: β-gallia.

The E_a values of the exothermic change in the coprecipitated samples decreased with an increase in the gallium content, while those in the mixed samples were nearly equal to that of the Ga-0 sample and scarcely changed at all in spite of the variation in the gallium content, as is shown in Table 4.

Table 4. Apparent activation energy for exothermic change around 900 °C

Sample	E_a, kcal/mol
Ga-0	243
Ga-7C	215
Ga-11C	209
Ga-14C	196
Ga-17M	227
Ga-19M	239

The Unit Cell Dimensions of the Mullite Formed in the Heat-treated Samples. The relationship between the unit cell volume, V, of the mullite heat-treated at 1200 °C for 5 hr and the gallium content in the original samples is shown in Fig. 3. The V of the mullite formed in the coprecipitated samples increased with an increase in the gallium content up to 15.25 wt% as Ga_2O_3, and then decreased above 17.72wt%, while those in the mixed samples scarcely changed at all in spite of variation in the gallium content in all except the Ga-18M sample.

The relationship between the unit cell length along the c axis, c_0, and the V of the mullite formed in the coprecipitated samples was approximately linear, as is shown in Fig. 4, in contrast to the case in the heat-treated mixed samples. Although the c_0 and V values of gallium-free mullite varied with the silica/alumina ratio,[13] the variation in the c_0 and the V of

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12) H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).

13) S. O. Agrell and J. V. Smith, *J. Amer. Ceram. Soc.*, **43**, 69 (1960).

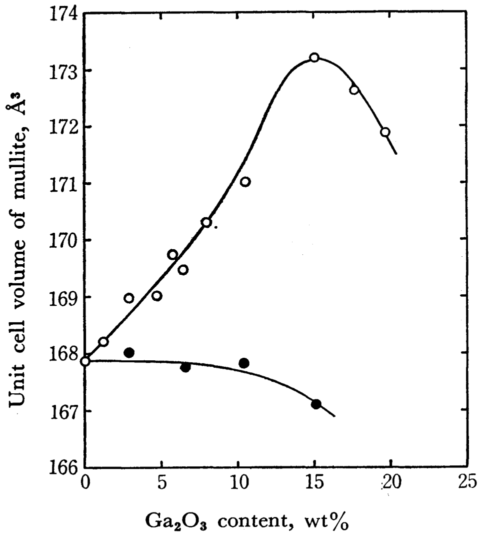

Fig. 3. Plot of unit cell volume of mullite formed at 1200 °C against gallium content.
○; coprecipitated samples, ●; mixed samples

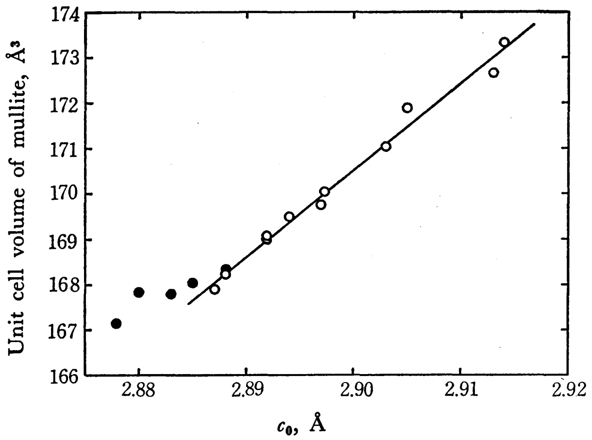

Fig. 4. Plot of unit cell volume against c_0 of mullite formed at 1200°C.
○; coprecipitated samples, ●; mixed samples

the mullite formed in the coprecipitated samples remarkably exceeded those caused by a change in the silica/alumina ratio.

Therefore, much of the gallium in the coprecipitated samples was considered to be included in the mullite by forming a solid solution, although a limit of the amount of gallium included in the mullite was obscure.

The maximum value of the V (173.3 Å^3, the Ga–8C sample) was larger than the reported value of the gallium-bearing mullite (170.1 Å^3).[5] However, it is difficult to compare them directly, since the substantial amount of gallium in the mullite formed in the Ga–8C sample can not be estimated.

Discussion

Because the exothermic peak around 900 °C in the DTA on the coprecipitated gels shifted continuously toward lower temperatures as the gallium content increased, the causes of all the exothermic peak must have the same pattern. The exothermic peak around 900 °C on the silica-alumina gel has been explanied as originating from the formation of mullite[14,15] or γ-alumina.[16] In the case of the coprecipitated gels with less gallium (*e.g.*, the Ga–1C and –3C samples), the results shown in Table 3 favor the conclusion that the formation of the mullite was responsible for this peak. On the contrary, the exothermic reaction product from the coprecipitated gels with more gallium (*e.g.*, the Ga–8C, –11C, and –13C samples) was found to be the silico-alumina spinel, similar to that of the Ga–14C sample, free from aluminum.

If the exothermic peak originates from the formation of the mullite, the inconsistency between a reduction in the apparent activation energy for the exothermic reaction and a rising trend of the crystallization temperature of the mullite with an increase in the gallium content can not be explained. A direct examination of the preheated samples indicated that the exothermic peak in the DTA resulted not only from the formation of the specified mineral, *i.e.*, mullite, but also from that of the silico-alumina spinel, which was a metastable phase. Furthermore, this exothermic peak is considered to originate in a structural change in the silica-alumina based gels, a change which arises from the formation of the mullite or the silico-alumina spinel, although its details are obscure; the kind of exothermic reaction products will depend on the composition, the coexistence state of gallium in the gels, and the crystallographic geometry.

The β-gallia formed was found to include aluminum ions as a solid solution, since the spacings of the β-gallia, one of the firing products in the gallium-rich coprecipitated samples and the aluminum-free one, decreased with the decrease in the gallium content. For example, the spacing for the (311) of the β-gallia[17] crystallized at 1200 °C in the Ga–11C, –12C, and –14C samples were 1.518, 1.529, and 1.545 Å respectively, while those in the two mixed samples, Ga–17M and –19M, were 1.542 and 1.545 Å respectively.

Judging from the chemical compositions and the results of the DTA and of the X-ray powder diffractometry of the heat-treated samples, the coprecipitated samples, the SiO_2–Al_2O_3–Ga_2O_3–H_2O system, prepared in this work are considered to be an allophane-like material, *i.e.*, a gallium-bearing allophane.

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14) T. Demediuk and W. F. Cole, *Nature*, **181**, 1400 (1953).

15) J. Ossaka, "Nendokagaku no Shinpo," Vol. 4, ed. by S. Iwao, Gihodo, Tokyo (1962), p. 33.

16) Y. Tsuzuki and K. Nagasawa, Ref. 15, p. 1.

17) The reported value for the (311) of the β-gallia is 1.542 Å; J. A. Kohn, G. Katz, and J. B. Broder, *Amer. Mineral.*, **42**, 398 (1957).