BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 972—982 (1967)

Thermo-Analytical Investigation of Phase Equilibria in the Al_2O_3-SiO_2 System

Toshiyasu HORIBE and Senzo KUWABARA
Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya

(Received June 9, 1966)

The phase equilibrium relation of the Al_2O_3-SiO_2 system was thermo-analytically investigated using a molybdenum resistance furnace with an argon atmosphere and a tungsten-tungsten 26% rhenium thermocouple (supplementary experiments were also made), and the phase diargam for the high aluminous region was presented. The composition of mullite with the highest melting point is $2Al_2O_3 \cdot SiO_2$ or very close to that value, and the mullite of the composition melts incongruently at 1890±5°C, giving a liquid with a composition slightly less in Al_2O_3 content than that of the mullite. Other investigators' results were interpreted on the basis of the results of the present investigation. In the present experiment an "unstable" growth of corundum was frequently observed.

The phase diagram on the Al_2O_3-SiO_2 system is an important one for the ceramic industry. In 1924 Bowen and Greig¹⁾ presented a new phase diagram in which mullite, melting incongruently at 1830°C (based on the International Temperature Scale of 1948), was given as a stable compound of this system instead of sillimanite. The diagram was widely accepted for many years. In 1951 a contradictory diagram was presented by Toropov and Galakhov²⁾; that is, they claimed

---

1) N. L. Bowen and J. W. Greig, *J. Am. Ceram. Soc.*, **7**, 238 (1924); corrections, *ibid.*, 410.

2) N. A. Toropov and F. Ya. Galakhov, *Doklady Akad. Nauk S. S. S. R.*, **78**, 299 (1951).

that the mullite melted congruently. Many investigations have been made, thereafter, of the melting behavior of mullite (*i. e.,* is it congruent or incongruent?). Nevertheless, it appears that the controversy on this problem is not yet over. The papers published previously can be classified into two groups according to their conception of the melting behavior of mullite, namely, the papers supporting Bowen and Greig's diagram1,3-5) and those claiming that the mullite melts congruently6-8) or that it melts incongruently giving corundum and a liquid of composition close to that of the mullite.9) Trömel *et al.*4) stated, on the basis of their own experimental results, that in the melting behavior of mullite a true equilibrium relation can be shown by a diagram similar to that of Bowen and Greig, while only an unstable relation was shown by the "congruent diagram." Aramaki and Roy7) and Budnikov and Kushakowskii,8) however, did not accept the Trömel opinion. Konopicky10) pointed out that the investigations supporting Bowen and Greig's diagram were different in heating atmosphere from the other investigations. From a survey of the papers on this problem, Müller-Hesse11) assumed that the melting behavior of mixtures of the system would depend on the heating condition and claimed that, hereafter, an attempt should be made to establish the relation between the heating conditions and the melting behavior.

Concerning the composition of mullite with the highest melting point, various values were reported. Values of 60,6) $61._5$,7) and 66.7 mol% $Al_2O_3$8) are found even in the papers claiming that the mullite melts congruently.

The present authors, interested in the phase diagrams necessary for manufacturing aluminous abrasives, investigated the phase equilibria of the Al_2O_3-Ti_2O_3 system using a molybdenum-resistance furnace.12) Knowledg of the phase equilibria of the Al_2O_3-SiO_2 system is also important for the abrasive industry. Therefore, an thermo-analytical investigation of this system was carried out using a molybdenum furnace filled with argon and a tungsten-tungsten 26% rhenium thermocouple. (The measurements in the present investigation were made mainly of melting behavior which can be examined by the thermo-analytical method. Concerning the solid solution region of mullite, only the composition of mullite with the highest melting point was exactly measured, and its boundaries were presumed.)

A thermo-analytical investigation of this system had been made previously by Budnikov and Kushakowskii,8) but the accuracy of their temperature measurement seemed not very good. The experimental conditions and the results of the present investigation will be described in detail, because the problem has been under controversial.

Experimental and Results

Materials. "S-Powder" of the Shinko Company and quartzite powder were used as the starting materials of aluminum oxide and silicon dioxide respectively. The "S-Powder was more than 99.9 % pure Al_2O_3, and the data of chemical analysis of the quartzite powder were as follows: SiO_2 99.55%, Al_2O_3 0.17%, Fe_2O_3 0.02%, CaO 0.05%, and ignition loss 0.18%.

Thermal Analysis. *Apparatus and Procedure.* Heatings were made in a molybdenum furnace filled with argon of about 1 atm. The argon was purified by passing it through silica-gel, diphosphorus pentoxide, copper mesh of 600°C, and titanium chips of 1000°C. The arrangement

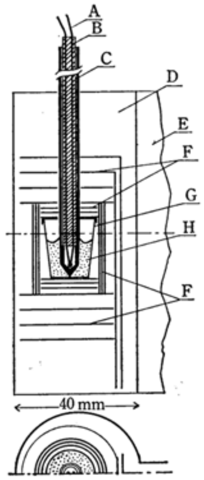

Fig. 1. Arrangement of sample and thermocouple. Mo heater is surrounded by radiation shields of Mo sheets.

A: W-W26Re thermocouple
B: ThO_2 insulating tube
C: Mo protecting tube
D: Mo heater
E: Power lead (to water-cooled copper electrode)
F: Mo sheets
G: Mo crucible
H: Sample

---

3) N. F. Filonenko and I. V. Lavrov, *ibid.,* **89**, 141 (1953).

4) G. Trömel, K.-H. Obst, K. Konopicky, H. Bauer and I. Patzak, *Ber. deu. keram. Ges.,* **34**, 397 (1957).

5) A. Neuhaus and W. Richartz, *ibid.,* **35**, 108 (1958).

6) N. A. Toropov and F. Ya. Galakhov, *Izbest. Akad. Nauk S. S. S. R.,* (1958), 8.

7) S. Aramaki and R. Roy, *J. Am. Ceram. Soc.,* **45**, 229 (1962).

8) P. P. Budnikov and V. I. Kushakowskii, *Zh. Prikl. Khim.,* **35**, 2146 (1962).

9) J. H. Welch, *Nature,* **186**, 545 (1960).

10) K. Konopicky, *Ber. deu. keram. Ges.,* **40**, 286 (1963).

11) H. Müller-Hesse, *ibid.,* **40**, 281 (1963).

12) T. Horibe and S. Kuwabara, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.),* **67**, 276 (1963).

of the sample and the themocouple in the furanace is shown in Fig. 1. (This arrangement was employed except in the R-series experiments.) The crucible and its cover were made of a molybdenum sheet; about 3.5 g of sample was taken. The electromotive force of the thermocouple was recorded with a recorder whose precision and sensitivity were ±0.025 mV and 0.005 mV respectively. The thermocouple was calibrated at the melting points of palladium, platinum, and rhodium by the method employed by Sata and Kiyoura.[13] Palladium wire, platinum wire, or a small compact of rhodium powder supported with tungsten wire was set very close to the hot junction of the thermocouple, and its melting was observed. The results of calibration are shown in Table 1. From the results a linear equation was used for the conversion of an electromotive force to a temperature between 1552°C and 2050°C. The shift of the electromotive force within the period of the present investigation was −0.05 mV at the melting point of aluminum oxide.

TABLE 1. ELECTROMOTIVE FORCE OF W-W26%Re THERMOCOUPLE AT MELTING POINTS OF STANDARD METALS

Standard metal (purity,* %)	Melting point °C	E.M.F., mV	
		measured	in catalogue
Pd (99.999)	1552	25.84±0.03	25.888
Pt (>99.99)	1769	29.94±0.04	30.210
Rh (99.999)	1960	33.48±0.03	33.588

* Presented by the supplier.

Toropov[2)] pointed out that the interpretation of the experimental results on this system was liable to error because of the vaporization of silicon dioxide during heating. In order to examine the vaporization during the heating of the present investigation, compacts of the mixtures of the system, each of which was kept in a covered molybdenum crucible, were heated in the furnace and the weight decrease was measured. The results are shown in Table 2. It is supposed that the vaporization rate during the thermal analysis would be higher than those shown in Table 2 because of the presence of a crevice between the protecting tube of the thermocouple and the hole of the crucible cover. The vaporization during the measurement, however, may be seen from the results shown in Fig. 2 to be little, the figure showing that the endotherm point did not change on repeated heatings.

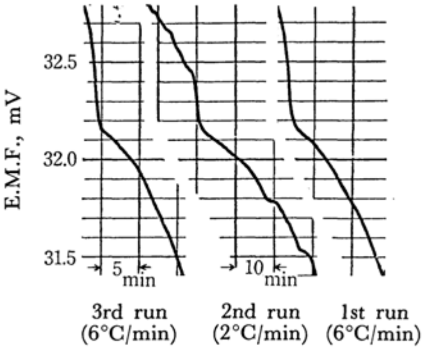

Fig. 2. Dependence of an endotherm point on heating rate. Heatings were repeated three times after setting a sample of 60 mol% Al_2O_3. Irregularity of the curve of the 2nd run at 31.53, 31.78 mV, *etc.*, were due to fluctuation of heating power of the furnace*.

* All the heating and cooling curves were checked by comparing them with the recorded voltage of the heating power.

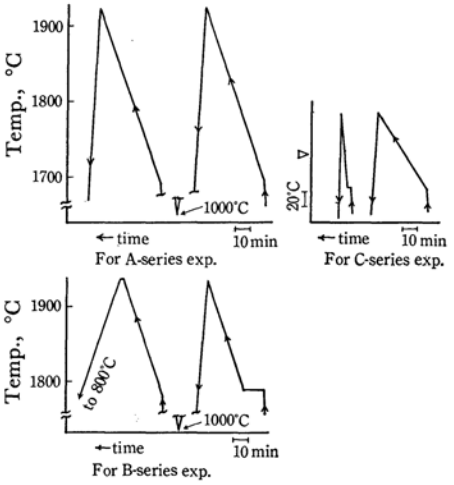

Fig. 3. Heating and cooling schedules of the thermal analysis.
(▷: Liquidus temp. of corundum at each composition)

Heating and cooling schedules of thermal analysis are shown in Fig. 3. A- and B-series experiments were made to obtain solidus of corundum or liquidus of mullite. C-series experiments were made to obtain liquidus of corundum. The heating rate was determined on the bases of the results shown in Fig. 2 and of the formation rate of mullite by the solid state reaction. The furnace was evacuated to about 3×10^{-5} mmHg after a sample had been set in it; it was then heated gradually to 1000°C, at which point the purified argon was introduced. Then the temperature was quickly raised, and measurements were made according to the schedule.

Results. Examples of the heating and cooling curves are shown in Figs. 4 and 5. The slight exotherm on the rapid cooling curves of B-68, -70, -72.5, and -75 was not found on the slow cooling curves (6°C/min) of the samples. The

---

13) T. Sata and R. Kiyoura, *Bull. Tokyo Inst. Tech.*, No. 53, 39 (1963).

TABLE 2. VAPORIZATION OF SiO_2

Sample*	Temp., °C	Duration of heating, min	Ratio of wt. decrease to initial SiO_2 content, %	Deformation of specimen
R-50-I	1790	30	0.2	Bottom of specimen adhered to crucible
R-50-II	1850	30	0.3	Softened
R-50-III	1910	20	0.3	Fused
R-65-I	1790	30	0.3	Only contraction
R-65-II	1850	30	0.4	Only contraction
R-65-III	1910	20	0.7	Fused
R-65-IV	1960	20	0.6	Fused

* Sign of sample: sort or series of experiment - number denoting the composition (Al_2O_3 mol%) - conditions of treatment.

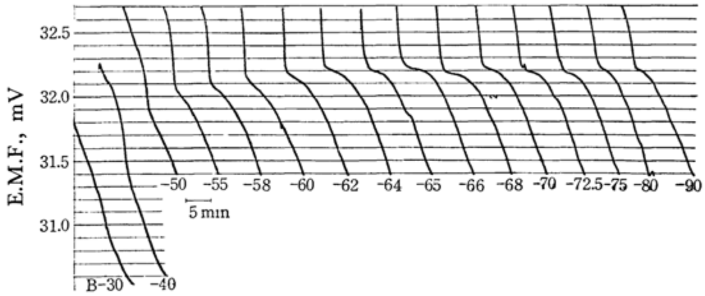

Fig. 4. Heating curves of B-series experiment.

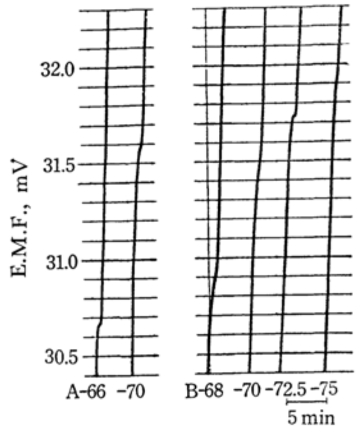

Fig. 5. Slight exotherm on the rapid cooling curves of A- and B-series experiments.

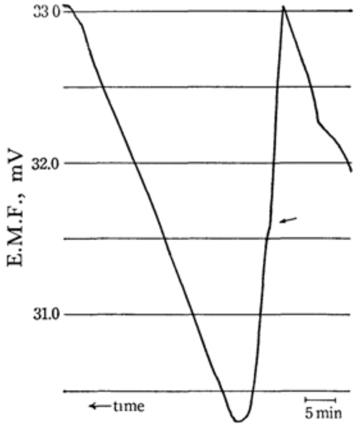

Fig. 6. The curve which shows that no endotherm occurred when the sample of 70 mol% Al_2O_3 was reheated as soon as slight exotherm (arrow) appeared.

sample of 70 mol% Al_2O_3 was reheated as soon as the slight exotherm appeared, as may be seen in Fig. 6. No endotherm occurred during the reheating, although the endotherm at the solidus of corundum appeared when the sample was reheated after having been cooled to 1000°C. The endotherm point and exothermic behavior at each composition are shown in Figs. 7 and 8. The endotherm points obtained in two runs of A- or B-series experiments were in good agreement at each composition. In C-series experiments a difference of less than 5°C was found between the endotherm points of two runs. Only a slight endotherm was found in the experiment on C-80. The endotherm point found on C-100, 100% Al_2O_3, was in good agreement with the melting point obtained by the method employed for the thermocouple calibration. A good reproducibility of the temperature at which a slight exotherm occurred during rapid cooling was found in A-66, A-70, C-80, or C-84, *i. e.,* within 5°C. The reproducibilities of the

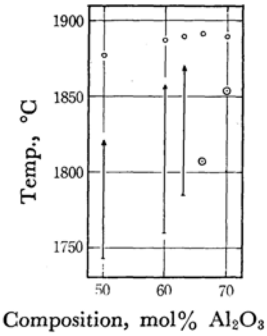

Fig. 7. Relation of composition *vs.* endotherm point (○) and exothermic behavior (⊙, arrow), which were obtained by A-series experiment. ⊙: Slight exotherm point, arrow: temperature recovery due to breaking of undercooling.

breaking temperature of undercooling and of the temperature recovered after the breaking were also good in each experiment, A-50, A-60, or A-63. The sample of A-66 was different from B-66 in its exothermic behavior during rapid cooling. Probably this difference was caused by the slight difference in composition. Our discussion will be based on the datum on B-66 because of its higher reliablity. The noticeable points in Fig. 8 are as follows; an abrupt change in exothermic behavior between B-66 and B-68 in the rapid cooling experiment, a lower exotherm or no exotherm at all in the slow cooling experiment of the samples of B-62 through B-66 in comparison with the exotherm in the rapid cooling experiment, and no exotherm in the rapid cooling experiments of B-80 and B-90.

Examination of the Sample after Thermal Analysis. Examinations were made also of the samples of R-series experiments.

Results of X-ray analysis are shown in Fig. 9. The samples of R′-68 and R′-70 shown in the figure were heat-treated at 1940°C for 20 min under the same setting of the sample as was used in R-series experiments. The noticeable points in the results are two; *i. e.*, an abrupt change in corundum content between B-64 and B-65, or between A-63 and A-66, and a lower corundum content of A-63 in comparison with the contents of B-62 and B-64.

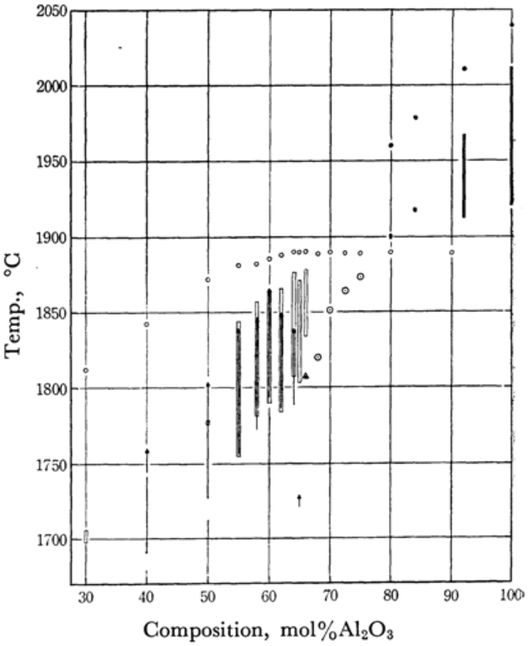

Fig. 8. Relations of composition *vs.* endotherm point and exothermic behavior, which were obtained in B- and C-series experiments.

Exp.	Endotherm pt.		Slight exotherm pt.	Temperature recovery due to breaking of undercooling
B-series	○	rapid cool	⊙	▭
		slow cool		⟶
C-series	●		■	▬

△: Slight exotherm pt. of A-66.

The lattice dimensions of mullite, shown in Table 3, were calculated from the diffraction angles of Cu$K\alpha_1$ radiation from (421), (002), and (250). Correction was made by employing an inner standard of pure silicon. As the separation of the $K\alpha_1$ and $K\alpha_2$ diffraction lines of (421) was insufficient in B-62, B-64, or R-50-III, the center of gravity of the composed peak was taken as the diffraction angle of $K\alpha$ radiation.

Microscopical observation was also made (Fig.

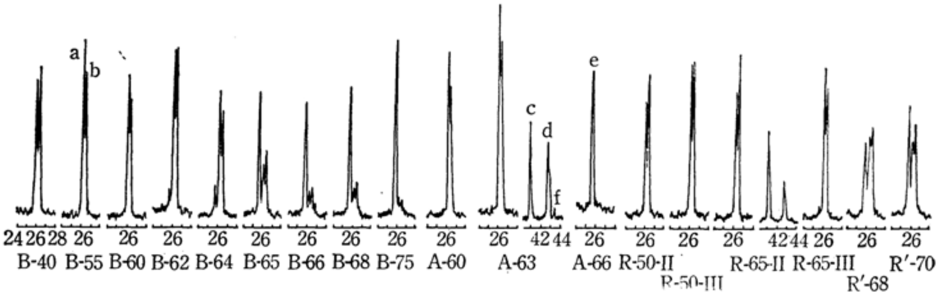

Fig. 9. X-Ray diffraction lines of the samples after A-, B- and R-series experiments (Cu$K\alpha$). Mullite: a (120), b (210), c (121), d (230); Corundum: e (102), f (113)

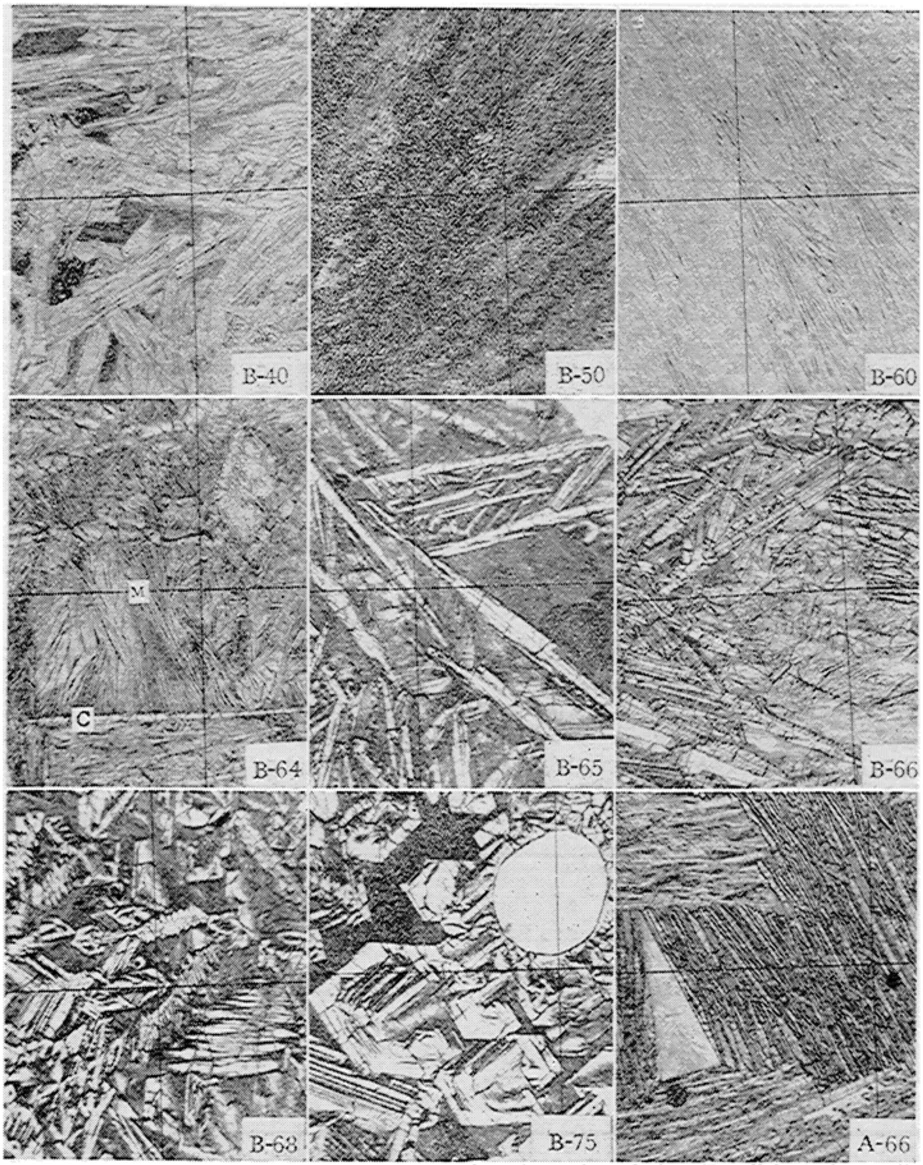

Fig. 10(a). Photomicrographs of the samples after thermal analysis. (Parallel nicols, ×40) In the photographs of B-65 through A-66 large crystals are corundum and matrices are glass containing fibrous crystallites. In B-64, 'C' is corundum and 'M' is mullite.

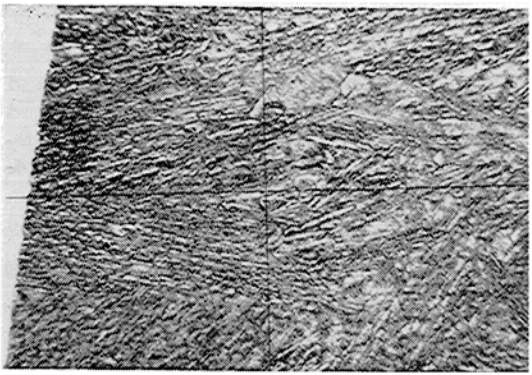

Fig. 10(b). Photomicrograph of R′-68 (Parallel nicols, ×40)

10). The abrupt changes between B-64 and B-65 and between A-63 and A-66 occurred also in the microstructure. A change in the shape of mullite is noticeable as well as a change in the corundum content. The shape of the corundum crystals are different according to the composition of sample; the crystals are elongated only to the direction parallel to its (0001) plane in B-62 and B-64. The triangle part of A-66 and the matrices of B-40 and B-66 were pale brown and slightly pleochroic. The maximum absorption was obtained when the elongated direction of fine fibres in the matrices coincided with the vibration direction of the polarized light. The brown matrix was observed also by Aramaki and Roy(7) and by Budnikov and

TABLE 3. LATTICE CONSTANTS OF MULLITE IN THE SAMPLES AFTER A-, B- OR R-SERIES EXPERIMENT
(Precision: a ±0.001—2Å, b ±0.0005Å, c ±0.0002Å)

Sample	Lattice constants, Å		
	a	b	c
A-60	7.569	7.684	2.8848
A-63	7.574	7.683	2.8849
B-40	7.556	7.685	2.8844
B-55	7.566	7.685	2.8847
B-60	7.569	7.685	2.8853
B-62	7.571	7.685	2.8852
B-64	7.571	7.684	2.8847
R-50-I	7.552	7.688	2.8841
R-50-II	7.557	7.685	2.8839
R-50-III	7.566	7.685	2.8847
R-65-I	7.565	7.685	2.8843
R-65-II	7.572	7.685	2.8852
R-65-III	7.581	7.682	2.8865
R′-68	7.566	7.684	2.8849
R′-70	7.567	7.688	2.8854

Kushakowskii.[8] From the results of the microscopical observation and X-ray analysis, it became clear that the breaking of undercooling, giving a large temperature recovery, was caused mainly by the crystallization of mullite, and that the slight exotherm shown in Fig. 5 was caused by the crystallization of corundum.

In sample of B-75 was taken as a representative of the samples containing a relatively large amount of corundum; its corundum content was thus determined. The sample (0.2 g) was treated with a mixture of hydrofluoric and sulfuric acids on a sand bath, and the residue was weighed after washing it by decantation. Its isolation was confirmed by a microscopical examination of the residue immersed in methylene iodide. The courndum content of the sample was found to be 63 wt%, from which the composition of the matrix was estimated to be 43 mol% Al_2O_3 and 57 mol% SiO_2. The corundum content of R′-68 was also measured; it was found to be 42 wt%.

Composition of the Mullite with the Highest Melting Point. The composition of the mullite with the highest melting point was presumed from Fig. 4 to be found between 66 and 68 mol% Al_2O_3. In order to determine the composition, compacts of a mixture of 75 mol% Al_2O_3 and 25 mol% SiO_2 were kept at 1880±4°C for 0.5 and 2 hr,[*1] and then rapidly cooled; the corundum content and the lattice constants of their mullite were then determined. The results are shown in Table 4. Photomicrograghs of their thin sections are shown in Fig. 11(a). Inclusions, the quantity of which could

TABLE 4. CORUNDUM CONTENT AND LATTICE CONSTANTS OF MULLITE OF THE SAMPLE OF 75 MOL% Al_2O_3 KEPT AT 1880°C

Sample	Corundum content wt%	Lattice constant, Å		
		a	b	c
S-75-0.5	28.7	7.579	7.681	2.8855
S-75-2	29.5	7.580	7.681	2.8858

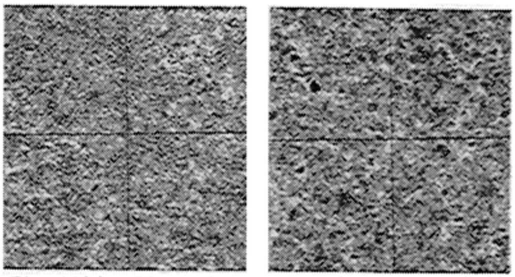

Fig. 11(a). Photomicrographs of S-75-0.5 (left) and S-75-2 (right). (Parallel nicols, ×100)

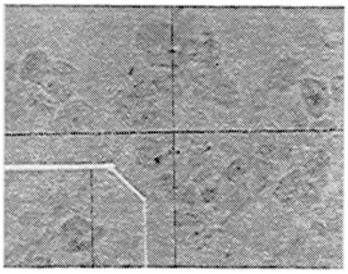

Fig. 11(b). Corundums isolated from S-75-2. Black spots are inclusions. (×400)

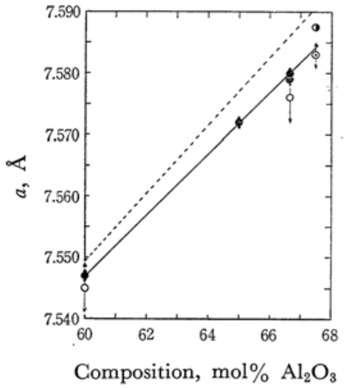

Fig. 12. Composition *vs.* lattice constant a of mullite.

- ● present investigation
- ⊙ Aramaki and Roy[7]
- ◑ Agrell and Smith (Forster mullite)[14]
- ○ Gelsdorf *et al.*[16]
- ··· Majumdar and Welch (for mullite prepared from melt)[15]

[*1] It took 10 min to heat it from 1000°C to 1830°C.

14) S. A. Agrell and J. W. Smith, *J. Am. Ceram. Soc.*, **43**, 69 (1960).

15) A. J. Majumdar and J. H. Welch, *Trans. Brit. Ceram. Soc.*, **62**, 603 (1963).

16) G. Gelsdorf, H. Müller-Hesse and H. E. Schweite, *Arch. Eisenhüttenw.*, **29**, 513 (1958).

be disregarded, were found in the corundum of these samples, as may be seen in Fig. 11(b). When the composition of the mullit formed is $2Al_2O_3 \cdot SiO_2$, the corundum content of the sample of 75 mol% Al_2O_3 is 27.9 wt%, which is very close to the measured values. In Fig. 12 a lattice constant, *a* of mullite*2 prepared from Korean kaolin and the constants of R-65-II, S-75-0.5, and S-75-2 are shown, together with those reported by other investigators, by assuming the composition of mullite in S-75-0.5 or -2 to be $2Al_2O_3 \cdot SiO_2$. In the samples examined in the present investigation, a linear relation was obtained between *a* and the composition, as is shown with a solid line in the figure.*3 The solid line is almost parallel to the other investigators'. The composition of the mullite with the highest melting point may be concluded to be $2Al_2O_3 \cdot SiO_2$, or very close to $2Al_2O_3 \cdot SiO_2$. (See also the data on Q-67 below.)

Melting Behavior of Mullite. Budnikov and Kushakovskii,8) and Toropov and Galakhov6) investigated the phase equilibria under similar heating conditions to those of the present investigation; they concluded that mullite (composition: $2Al_2O_3 \cdot SiO_2$,8) $3Al_2O_3 \cdot 2SiO_2$6)) melted congruently, and that the composition of eutectic point between corundum and mullite was more than $67._5$ mol%8) or 69 mol%6). The foregoing results, shown in Fig. 4, are inconsistent with their conclusion. Therefore, we re-examined the melting behavior by another method. Mixtures of Al_2O_3 68 mol% and of Al_2O_3 75 mol% were heated as are shown in Fig. 13, and the corundum contents of the samples cooled rapidly were determined. The microscopical examinations was also made (Fig. 14). By comparing Fig. 14 with Fig. 11, it may be found that corundum crystals grew remarkably during the heating. From this fact it may be supposed that the mass transport velocity in the melt was fairly large, so that the equilibrium state was attained in the mixtures at least at the solidus temperature of corundum. The corundum contents of Q-68 and Q-75 were found to be 11.1 wt%. and 29.5 wt% respectively. From these values, the Al_2O_3 contents of the matrices of Q-68 and Q-75 were estimated to be $64._6$ mol% and $66._0$ mol% respectively. These Al_2O_3 contents are lower than that of the mullite with the highest melting point. If the "unstable growth of corundum"18) (*cf.* the next chapter) did not occur in these experiments, it may be concluded that mullite melts incongruently. The results of the following experiments will indicate that the "unstable growth" would not occur.

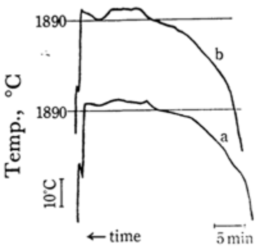

Fig. 13. Heating curves of Q-68(a) and Q-75(b) Exotherm found in cooling curves is due to crystallization of mullite.

In the first series of the supplementary experiments, the samples of 66 mol% Al_2O_3 (Q-66) and 67 mol% Al_2O_3 (Q-67) were heated according to approximately the same schedule as used for those shown in Fig. 13 and examined. Corundum was not detected by X-ray analysis or microscopical observation in either sample. The lattice constants of the mullite of the samples are shown in Table 5, together with those of Q-68 and Q-75.

In the second series, the samples of 66, 67, 68, and 75 mol% Al_2O_3 (L-66, L-67, L-68, and L-75 respectively) were heated at 2°C/min from 1830°C up to the corundum solidus, kept at that temperature for times of from 10 to 30 min, heated at 1895°C for 20 min, and then cooled rapidly. The presence of corundum was examined and the lattice constant of mullite were measured in the upper part and the lower part of each sample. The results are presented in Table 6. In the samples of L-66, L-67, and L-68, corundum settled, probably because of the long duration of heating above the corundum solidus temperature. The corundum in L-66, the amount of which was very small, must have been formed on the surface of the melt by the vaporization of silicon dioxide and then have settled. The corundum content of the lower part increased in the order of L-66, L-67, L-68.

TABLE 5. LATTICE CONSTANTS OF MULLITE IN SAMPLES OF Q-SERIES

Sample	Lattice constants, Å		
	a	*b*	*c*
Q-68	7.584	7.683	2.8867
Q-75	7.585	7.683	2.8867
Q-66	7.584	7.682	2.8865
Q-67	7.591	7.681	2.8869

---

*2 This mullite was prepared by heating Korean kaolin at 1500°C for 3 hr and then treating it with dilute hydrofluoric acid. Its composition was $3Al_2O_3 \cdot 2SiO_2$17) (*b*: 7.689 Å, *c*: 2.8851 Å). The authors wish to thank Dr. Okuda of our Institue for supplying this mullite.

17) H. Okuda, S. Kato and T. Iga, *Nagoya Kogyo Gijutsu Shikenjo Hokoku (Rept. Gov. Ind. Research Inst., Nagoya)*, **11**, 193 (1962).

*3 Aramaki7) stated that the change in the *a* of mullite due to the change in composition from $3Al_2O_3 \cdot 2SiO_2$ to $2Al_2O_3 \cdot SiO_2$ was only 0.01 Å. It is difficult, however, to accept his statement; the argument against his statement will be made in the next chapter.

18) W. Eitel, "Silicate Melt Equilibria," Rutgers Univ. Press, New Brunswick, New Jersey (1951), Pars. 23 and 38.

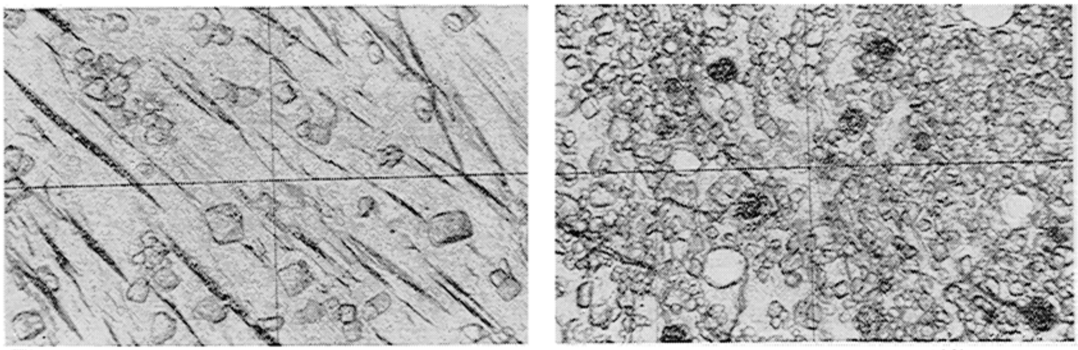

Fig. 14. Photomicrographs of Q-68 (left) and Q-75 (right). (Parallel nicols, ×100)
Grain: corundum, Matrix: mullite

TABLE 6. EXISTENCE OF CORUNDUM AND LATTICE CONSTANT OF MULLITE IN SAMPLES OF L-SERIES

Sample		Existence of corundum	Lattice constant *a*, Å
L-66	upper	non	7.588
	lower	found	7.590
L-67	upper	non	7.590
	lower	found	7.587
L-68	upper	non	7.589
	lower	found	7.583
L-75	upper	found	7.585
	lower	found	7.585

As for the lattice constant, *a*, of mullite shown in Table 6, it should be noticed that the *a* of the parts containing a larger amount of corundum is smaller than that of the other parts. This was caused probably by the crystal growth of corundum during the cooling.

Now, let us consider whether the "unstable growth of corundum" occurred or not in the L-series samples. The composition of the clear parts of the L-series samples is considered to be the composition of the liquid in equilibrium with corundum at 1895°C and is estimated to be about 67 mol% Al_2O_3 by comparing the lattice constant, *a*, with that of Q-67. When corundum liquidus is elongated to the corundum solidus through the point of 67 mol% Al_2O_3 and 1895°C on the phase diagram (see Fig. 15), it crosses the solidus at 66 mol% Al_2O_3. The composition at the cross point agrees with that of the mullite of the parts containing a large amount of corundum, which may be estimated by comparing the *a* with that of Q-66. This agreement suggests that the corundum grew to the peritectic point along the equilibrium relation; it may be considered that the "unstable growth of corundum" did not occur in the L-series samples, and also in Q-68 or Q-75. (It is supposed that the clear parts were obtained owing to the lack of the nucleus corundum.)

It is probable that the mullite with the highest melting point melts incongruently, givein a liquid of 66 mol% Al_2O_3 and 34 mol% SiO_2 or of composition very close to that value.

It should be noticed that the lattice constant of the mullite formed by rapid cooling of melt is slightly different from that of "sintering" mullite (*e. g.*, S-75).

Phase Diagram and Discussion

Figure 15 is a proposed phase diagram, the solid lines in which were drawn according to the endotherm points. The peritectic point was determined by the Q- and L-series experiments. The presumed solid solution region of mullite is shown with broken lines. The value obtained with S-75 is employed as the composition of mullite with the highest melting point. The boundary of the SiO_2 side was presumed from the compositions of mullite in the samples of R-50-I and R-50-II. The mullite compositions were estimated, using the relation shown in Fig. 12 with the solid line, from the value

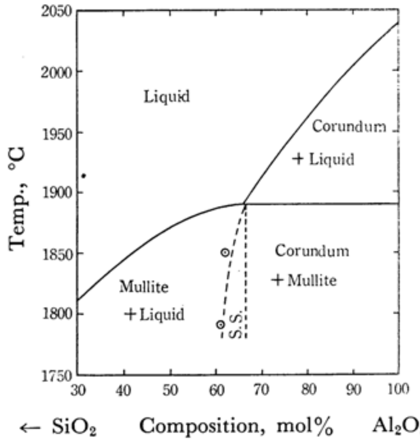

Fig. 15. Phase diagram of high aluminous region of the system Al_2O_3–SiO_2.
S.S.: Solid solution of mullite,
⊙: Composition of mullite in R-50-I or R-50-II

of *a*. The report of Gelsdorf *et al.*[16] was referred to for drawing the Al_2O_3 side boundary of the region, because the abrupt change in exothermic behavior on rapid cooling between B-66 and B-68 could be successfully interpreted by using their data.

The following observations, namely, a) the presence of a large amount of corundum in A-66 and in the B-series samples containing more than 65 mol% Al_2O_3, and b) the presence of corundum in B-62 and B-64, cannot, however, be predicted from the proposed phase diagram. These observations can not be explained only by the composition shift due to the vaporization of silicon dioxide, because its vaporization rate was not high (*cf.* Table 2 and Fig. 2). It has been recognized that, in certain silicate systems, corundum was apt to be "unstably" crystallized because of its high crystallizability.[18] The a) observation may be successfully explained in terms of the "unstable growth" of the corundum crystals formed in its stable region in the proposed phase diagram, although the formation of the nucleus corundum in B-65 should be attributed to the slight vaporization of silicon dioxide. It may be supposed that the unstable growth proceeded along the prolongation of the corundum liquidus beyond the peritectic point.[18] The corundum in B-62 or B-64 would be formed by the unstable growth of the small corundum crystals which were formed on the surface of melt by the slight vaporization of silicon dioxide. When the samples of B-66 through B-90 were cooled rapidly, B-66 entered quickly into the stable region of mullite after a brief exposure to the stable region of corundum, while the samples of B-68 through B-90 entered into the region where the two crystalline phases co-exist, where corundum would be crystallized predominantly. Therefore, the abrupt change in exothermic behavior, namely, the abrupt change in the principal crystalline phase formed, would occur between B-66 and B-68.

The slight exotherm during the rapid cooling, which was found on the samples of B-68 through B-75, did not appear in the experiments on B-80 and B-90. It may be presumed that the slight exotherm was caused by the sudden deposition of corundum due to the breaking of the supersaturation (see Fig. 6 and the phases in A-66). The lack of a "slight exotherm" in B-80 and B-90 may be explained by the fact that 1940°C, the top temperature in the B-series experiments, was below the liquidus of corundum at these compositions.

It should be noticed that in Q-68 and Q-75, which were heated up to a temperature only slightly higher than the corundum solidus, mullite crystallized rapidly in spite of the presence of corundum. It is probable that the rapid crystallization of mullite was caused by the survival of an "embryo-like" structure of mullite in the melt. In the many other experiments of the present investigation, corundum grew unstably. It may be presumed that the unstable growth of corundum crystals in these experiments was caused by the destruction of the "embryo-like" structure of mullite; that is, the "embryo-like" structure in the melt was broken due to the higher heating temperature or the longer duration of the heating, and the formation of the mullite nucleus was suppressed.

The phase diagram shown in Fig. 15 is approximately in accord with that of Welch[9] except the solid solution region of mullite. Welch investigated by using a high temperature microscope. The eutectic between corundum and mullite, which was reported by Budnikov[8] or by Toropov,[6] could not be found, as has been described before.

Konopicky described that the phase equilibrium relation of this system may be changed by the heating atmosphere.[10] In the following, the other investigators' results will be interpreted on the basis of the present results, by setting aside the Konopicky opinion provisionally. Aramaki and Roy[7] reported that the solid solution region of mullite was relatively narrow (from $60._3$ mol% to 63 mol% Al_2O_3 at 1840°C), and that the mullite composition giving the highest melting point was about $61._5$ mol% Al_2O_3. These results are incompatible with the present results. They considered that $2Al_2O_3 \cdot SiO_2$ mullite was a metastable phase which could be formed only by the solidification of melt, and they took its metastability as a supplementary evidence for the narrow solid solution region of mullite. The mullite of $2Al_2O_3 \cdot SiO_2$ was formed, however, by a sintering process in the present investigation (S-75-0.5 and -2), and also in the investigation of Gelsdorf *et al.*[16]; that is, this mullite is not a metastable phase, but a stable one. Aramaki and Roy reported also the results shown on Table 7 and described the difference of *a* corresponding to the heating temperature as being attributable largely to the heating temperature itself. It is difficult, however, to accept their statement without data on the chemical composition of mullite itself. Even when the Aramaki's statement is accepted, the composition of mullite in the mixtures prepared by Aramaki at 1790°C could be estimated from their lattice constant, *a*,

TABLE 7. RELATION OF HEATING CONDITION *vs.* LATTICE CONSTANTS *a* OF MULLITE (AFTER ARAMAKI AND ROY[7])

Composition of mixture, mol%Al_3O_3	Heating condition	*a* Å
50	a)	7.538±0.003
55	b)	7.566±0.002
67	a)	7.548±0.003
67	b)	7.574±0.002

a) 1300±50°C for 60 days
b) 1790±30°C for 40 min

using the relation shown in Fig. 12, since the solid line in Fig. 12 was drawn using the lattice constants of R-65-II and S-75, which were prepared at temperatures close to 1790°C.[*4] The compositions of mullites in the mixtures of 67 mol% Al_2O_3 and of 55 mol% Al_2O_3 prepared by Aramaki were estimated to be 65.4 and 63.8 mol% Al_2O_3 respectively. The former value is closer to 66.7 mol% than to 63 mol%. The latter value almost coincides with the mullite solidus in Fig. 15 if it is permissible to shift Aramaki's temperature scale to that of the present investigation by employing the melting point of mullite as a datum-point. The investigators supporting Bowen and Greig's diagram,1) *i. e.,* Trömel *et al.*4) and Neuhaus and Richartz,5) stated that true equilibrium (above the peritectic point, 1830°C) was attained only after prolonged heating because of the high stability of mullite. Neuhaus and Richartz heat-treated the single crystal of $2Al_2O_3 \cdot SiO_2$ mullite, which was grown by the flame-fusion process, at 1870±15°C for 0.5 1.5, and 4 hr in a normal atmosphere; they stated, after an examination of the samples, that the formation of corundum and the contraction of *a* and *b* of mullite due to the composition shift towards $3Al_2O_3 \cdot 2SiO_2$ proceeded with the duration of heating. However, their statement is very questionable, because in their data (Column 5 of Table 4 and Table 5) it is found that the lattice spacings of (201) and (311), being more sensitive to the concentration of Al_2O_3, of the single crystal mullite did not change even after heating for 4 hr. Accordingly, it seems improper to accept their experimental results as evidence of the unstability of mullite at the temperature. Trömel *et al.* heated Al_2O_3-SiO_2 mixtures of various compositions at 1830°C for 6 hr and found only corundum and glass in the specimens containing more than 55 wt% Al_2O_3. They observed also that, when these specimens were reheated to melting and cooled rapidly, other phases, the formation of which are not contradictory to the present phase diagram, appeared. Their detection of corundum even in mixtures containing a relatively low amount of Al_2O_3 after heating for 6 hr may be explained by the unstable growth of the corundum formed by the vaporization silicon dioxide (or of corundum of the plate for sample setting), since they stated that the accuracy of temperature control during the heating was not high. This explanation is supported by the estimated value of the composition of the matrix in B-75, Al_2O_3 43 mol% and SiO_2 57 mol%.

The authors wish to thank Messrs. Shigeru Katto, Shiro Watanabe, and Hiroshi Yamada for their help.

[*4] Although a difference is found in the chilling rate, it could be disregarded since Aramaki showed that the *a* of the arc-fusion mullite shifted only slightly by a heat treatment (comparable to the range of experimental error). It is probable that the homogenization of the arc-fused mullite by the heat treatment, which was described by them, did not affect the lattice constant, because the initial quantity of the inclusion was less than 0.1 vol%.