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Phase relations of cordierite and sapphirine in the system MgO-Al_2O_3-SiO_2

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Cordierite and corundum (α–Al_2O_3) are shown to be compatible phases below 1386 ± 5° C. The reaction cordierite + corundum = mullite + spinel is reversible, but sluggish. Na_2O and CaO (1.5 wt %) extend the stability of assemblages with mullite and spinel to slightly lower temperatures: 1364 ± 5° C and 1380 ± 8° C respectively, while 1.5 wt % iron oxide raises their stability temperature to 1397 ± 8° C.

1. Introduction

Rankin and Merwin [1] found cordierite, $Mg_2Al_3Si_5AlO_{18}$, to be the only ternary phase in the MgO–Al_2O_3–SiO_2 system. However Foster [2, 3] subsequently showed that a second ternary phase, sapphirine, occurred: it has the approximate formula $Mg_4Al_{10}Si_2O_{23}$. Because synthetic sapphirine melts incongruently to spinel and liquid, Foster reasoned that sapphirine must have a stability field at the liquidus and he presented several schemes compatible with the available experimental evidence. Keith and Schairer [4] subsequently showed which scheme was correct and their conclusions are accepted in critical compilations such as that of Muan and Osborn [5].

Foster also presents evidence that at subsolidus temperatures the stability relations of sapphirine with mullite, spinel and corundum undergo a change at about 1460° C. This is shown schematically in Fig. 1a and b: above 1460° C, spinel and mullite are compatible phases, whereas below 1460° C, sapphirine and corundum constitute the more stable pair. These figures omit several small two-phase regions: for example, at ~ 1460° C, both spinel and mullite will have a variable composition but the existence of these solid solutions, while tending to reduce somewhat the ranges of bulk compositions which lie in the three-phase regions, does not alter the essential argument presented here: namely that the stable pattern of phases present in both two- and three-phase regions undergoes a second major alteration at temperatures below 1460° C.

Credit for this discovery belongs to Boden [6] who, in the course of studying the crystallization of TiO_2-nucleated compositions, noted that cordierite and corundum appeared to coexist under conditions which were believed to represent equilibrium. To eliminate possible complications due to the presence of TiO_2, some experiments were also made on MgO–Al_2O_3–SiO_2 compositions: this evidence supported the hypothesis that at temperatures below ~ 1390° C, cordierite and corundum co-existed. Unfortunately, in the time available to him it was not possible to obtain absolutely conclusive proof. As cordierite–alumina ceramics are widely used in catalyst support systems the relative stabilities of these phases seemed to warrant further study, and we now report the results obtained.

2. Experimental

Two sets of starting materials were used, the first consisting either of fine-grained mechanical mixtures and glasses prepared from these; the second, gels. The mechanical mixtures were made from "Analar" MgO, "Cera" Al_2O_3 and ground quartz containing 99.9% SiO_2. The total impurity content was ~ 0.1%. Some compositions having liquidus temperature $\leqslant 1600°$ C were fused to glasses in Pt crucibles. The gels were made by ammonia coprecipitation of alcoholic solutions of Mg and Al nitrates ("Analar") and ethyl orthosilicate; the gels are also to be distinguished from the other starting materials by their greater impurity content (~ 0.2%). The nitrate-containing gels were decomposed at the lowest possible temperature by gentle ignition.

Samples of these materials, enclosed in Pt foil, were heated in temperature-controlled furnaces. Preliminary runs were made in muffle furnaces (± 10 to 15° C) but all the determinations shown in the Tables were made in vertical-tube furnaces whose estimated accuracy of control and measurement was ± 2 to 3° C in runs of short duration (1 to 100 h) but probably only ± 3 to 4° in longer runs (500–1000 h). The phases present were identified using a Hägg Guinier X-ray camera with Cu*K*α radiation.

3. Results

3.1. Liquidus invariant points of cordierite and sapphirine

The crystallization of 15 compositions, initially prepared both as glasses and sinters was studied. We found no reason to doubt that the location (within ± 1.0 wt %) and nature of each of the invariant points shown by Keith and Schairer are correct. To eliminate differences arising from changes in temperature scales, the "literature" values cited are taken from Muan and Osborn, who have corrected earlier values uniformly to the 1968 I.P.T.S. Some differences between the tem-

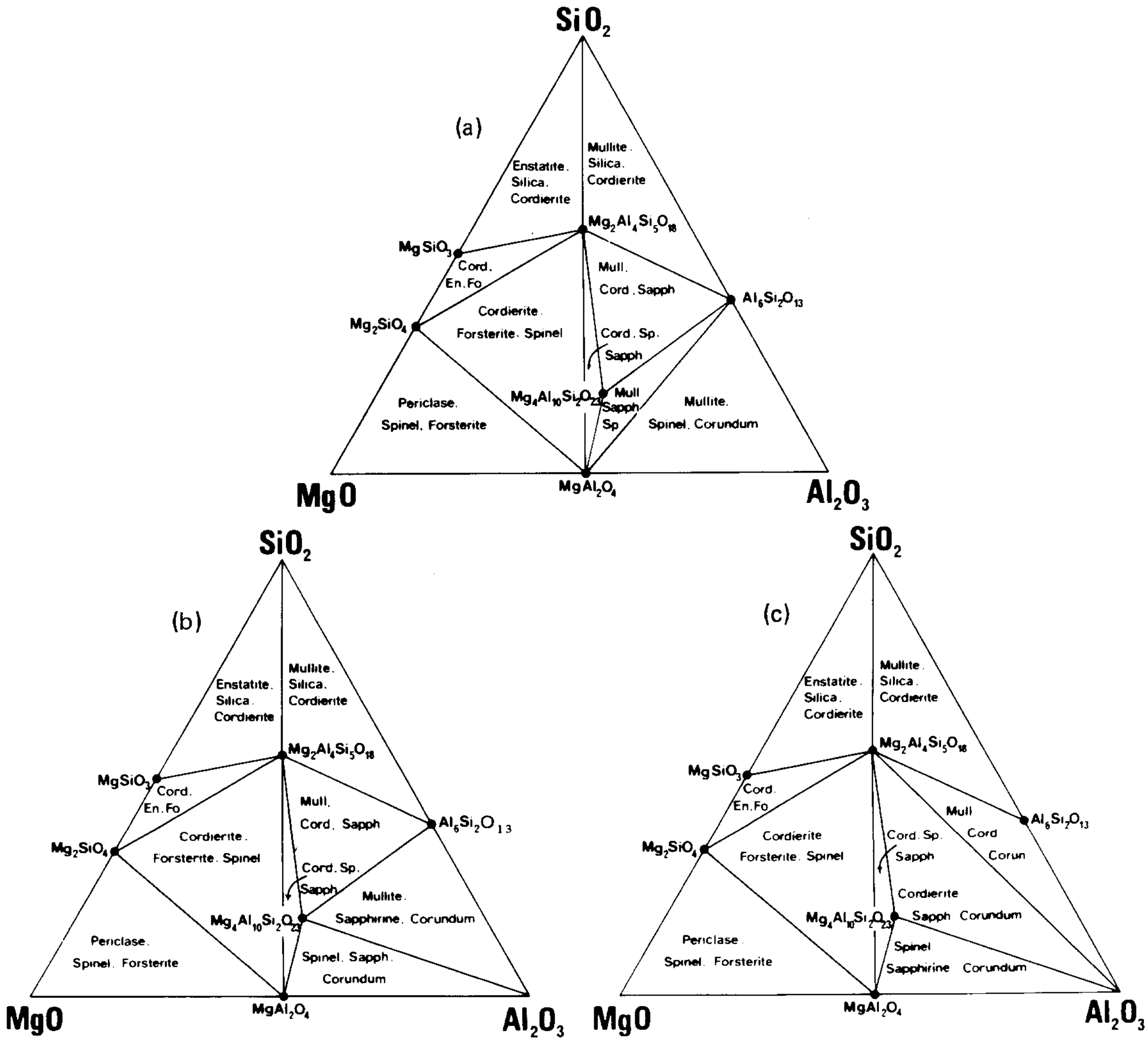

Figure 1 Phase distributions in the system $MgO-Al_2O_3-SiO_2$: (a) As inferred from the liquidus invariant points: the mullite–spinel join is stable only above 1460° C. (b) As above, but showing a stable join between sapphirine and mullite which exists between 1386 and 1460° C. (c) Below 1386° C. The polymorphic of form(s) $MgSiO_3$ and SiO_2 are not distinguished separately hence the use of "enstatite" and "silica" respectively. The diagrams omit the ranges of composition of cordierite, sapphirine, spinel, and mullite and show only the three-phase regions.

TABLE I Liquidus invariant points of cordierite and sapphirine

Nature of point and phases present with liquid	Temperature (° C)	
	This study	Literature
P_1 : cristob., mull., cord.	1444 ± 2	1440
E_1 : cristob., protoenst., cord.	1345 ± 2	1355
M_1: protoenst., cord.	1363 ± 2	1367
E_2 : forst., protoenst., cord.	1360 ± 2	1365
P_2 : forst., spinel, cord.	1373 ± 2	1370
P_3 : sapph., spinel, cord.	1448 ± 2	1453
P_4 : sapph., mull., cord.	1454 ± 2	1460
M_2: cord., mull.	1457 ± 2	1465
P_5 : sapph., spinel, mull.	1469 ± 2	1482
P_6 : mull., corundum, spinel	1560 ± 15	1578

Abbreviations: E = eutectic, M = maximum, P = peritectic. Cristob. = cristobalite, SiO_2, Mull. = mullite, Cord. = cordierite, Protoenst. = protoenstatite, $MgSiO_3$, Forst. = forsterite, Mg_2SiO_4, Sapph. = sapphirine.

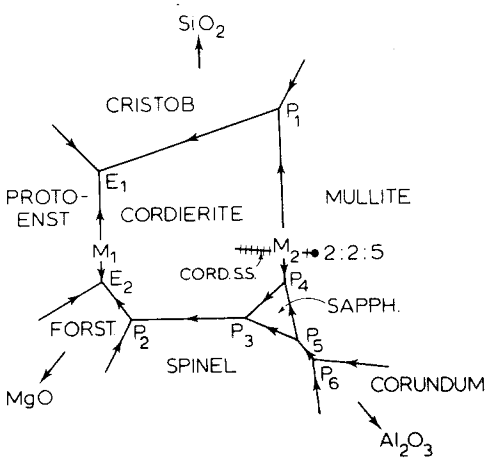

Figure 2 Schematic diagram showing the arrangement of liquidus invariant points bordering the primary phase fields of cordierite and sapphirine. The cross-hatched line extending from the ideal (2:2:5) cordierite composition shows the range of cordierite solid solutions. Data for the invariant points are given in Table I.

TABLE II Subsolidus reactions bearing on the stabilities of sapphirine–mullite–cordierite–corundum assemblages. Composition: $15MgO–60Al_2O_3–25SiO_2$ (wt %)

Temperature (° C)	Time (h)	Phases present
(a) Temperature > 1386° C: gel and mechanical mixtures.		
1389	48	cord., corundum, sapph., U.
1391.5	96	cord., corundum, sapph.
1395	144	cord., corundum, sapph., mull (tr.)
1391.5	192	cord., corundum, sapph., mull.
1391.5	240	cord., sapph., mull., corundum (tr.)
1391	312	cord., sapph., mull., corundum (tr.), X (tr.)
1390	582	cord., sapph., mull., corundum (tr.), X
1391	1000	cord., sapph., mull., X (tr.)
(b) Temperature < 1386° C: gell and mechanical mixture.		
1382	48	cord., corundum, sapph., U
1382	96	cord., corundum, sapph.
1380	144	cord., corundum, sapph.
1380	192	cord., corundum, sapph., X (tr.)
1381	300	cord., corundum, sapph., X
1381	580	cord., corundum, sapph., X
(c) Temperature > 1386° C: mixture of cordierite, corundum sapphirine and X prepared by heating a mechanical mixutre for 580 h at 1380° C.		
1395	24	cord., corundum, sapph., X
1395	72	cord., corundum, sapph., X, mull. (tr.)
1392	168	cord., corundum, sapph., X, mull.
1392	350	cord., corundum (tr.), sapph., X, mull.
1392	700	cord., sapph., mull., X
(d) Temperature < 1386° C: mixutre of cordierite, sapph., mullite and corundum (trace) prepared by heating a mechanical mixture for 168 h at 1400° C.		
1368	24	cord., sapph., mull., corundum (tr.)
1368	96	cord., sapph., mull., corundum (tr.)
1370	168	cord., sapph., mull., corundum
1372	336	cord., sapph., corundum, mull. (tr.)
1372	500	cord., sapph., corundum

Notes and abbreviations: U = other phases (described in text) tr = trace. Remaining abbreviations, same as in Table I. Phase X is an incompletely characterized phase which is described in the text.

peratures reported for the invariant points remain: these are compared in Table I, which should be read in conjunction with Fig. 2. Thus, we find the temperature of the peritectic with sapphirine, spinel and liquid to be 13° C lower than the literature value. Our determination of the temperature of the eutectics with SiO_2 yielded both cristobalite and tridymite as phases of crystalline silica co-existing with liquid.

3.2. The reaction: sapphirine + mullite = cordierite + corundum

Evidence that this reaction is reversible at 1386 ± 5° C is summarized in Table II. Proof was obtained in two ways: first, by determining the reaction products of gel or crystalline starting materials reacted above and below 1386° C and second, by annealing mixtures containing sapphirine and mullite *below* 1386° C as well as mixtures containing cordierite and corundum *above* 1386° C. The products obtained by reaction above 1386° C are in accord with Foster's data; therefore, we confirm the phase distributions shown in Fig. 1b. However, below 1386° C, the distribution of phases is shown in Fig. 1c.

After 48 h, the gel mixture gave much Mg-petalite (a phase having a structure like that of high quartz) whereas the mechanical mixture gave enstatite, silica, etc, amongst the products of incomplete reaction. However, after 96 h, differences between the phases present has largely disappeared owing to the consumption of those metastable phases formed during the earlier stages of reaction. With increasing time, it can be seen that above 1386° C cordierite, sapphirine and mullite continue to develop whereas below 1386° C, cordierite, corundum and sapphirine form. Both the gels and mechanical mixtures also gave a small quantity of hitherto-unknown phase, designated "phase X": its powder X-ray pattern, obtained by subtraction of reflections due to cordierite, etc, is shown in Table III. Phase X appears only in compositions which had previously crystallized cordierite: it is believed that this cordierite departs from the ideal 2:2:5 composition, and that X is subsequently produced as an exsolution product. Its compositions is, as yet, unknown. In the runs of longest duration (~ 1000 h) phase X, while still present, appears to be diminishing in quantity and we have therefore not taken it into account in depicting the equilibrium phase relations although it was present, at least in traces, in almost all of our annealed preparations.

TABLE III Powder reflections for phase X

d (Å)	*I*
6.17	m
4.24	w
3.89	s
3.78	m
3.66	m
2.60	w

A preparation heated 580 h at 1380° C containing initially cordierite, corundum and sapphirine, together with a little X, was heated above 1386° C: after heating the corundum had disappeared while mullite formed. On the other hand, when heating the same composition below 1386° C – the initial products consisting principally of cordierite, sapphirine and mullite, together with a trace of unreacted corundum – it was found that mullite vanished while corundum appeared.

Thus, it has been demonstrated that the reaction is reversible, albeit slowly, at 1386 ± 5° C.

3.3. Effect of CaO, Na_2O, and iron oxides on the reaction: sapphirine + mullite = cordierite + corundum

The effects of these oxides were investigated by taking a sinter, prepared at ~ 1360° C, which contained cordierite, corundum and sapphirine. Samples of this were used as "controls". To portions of this were also added Na_2CO_3, $CaCO_3$ or Fe_2O_3 equivalent to 1.5 wt% respectively of Na_2O, CaO or Fe_2O_3. After blending, these samples were reheated at various temperatures between 1360 and 1410° C: the phases present are shown in Table IV. The appearance of mullite is a sensitive indication that with rising temperatures the cordierite–corundum–sapphirine assemblage has become unstable with respect to the assemblage cordierite–mullite–sapphirine. The reactions did not go to completion in the time allowed and the presence of Na_2O, CaO or iron oxide did not significantly alter the kinetics of reaction: to obtain essentially complete reaction would have required ~ 10^3 h. Na_2O and CaO lower the temperature of the four-phase reaction to 1364 ± 5° C and 1380 ± 8° C respectively while iron oxide – undoubtedly present as both Fe^{2+} and Fe^{3+} – raises this temperature to 1397 ± 8° C. The addition of 2.5% Fe_2O_3 resulted in a further slight increase in the temperature of the four-phase reaction to 1408 ± 3° C: liquid was also present.

TABLE IV Effect of Na_2O, CaO and iron oxide on the reaction: sapphirine + mullite = cordierite + corundum

Temperature (° C)	Time (h)	Control	1.5% Na_2O	1.5% CaO	1.5% Fe_2O_3
1405	120	cord, (cor) sapph., *mull*	–	–	cord, (cor) sapph., *mull*
1389	168	cord, (cor) sapph., *mull*	cord, (cor) sapph., *mull*	cord, (cor) sapph., *mull*	unchanged
1372	168	unchanged	cord, (cor sapph., *mull*	cord, (cor) sapph., *mull*	unchanged
1368	168	unchanged	cord, (cor) sapph., *mull*	unchanged	unchanged
1360	300	unchanged	unchanged	unchanged	unchanged

Starting material: composition $15MgO–60Al_2O_3–25SiO_2$ (wt %) containing cordierite, corundum and sapphirine. The control sample was of the sinter itself. 1.5% of Na_2O (as Na_2CO_3), Cao (as $CaCO_3$) and Fe_2O_3 (as Fe_2O_3) were intimately mixed with portions of this sinter and reheated. Phases appearing as a result of the heat-treatment are in italics; those diminished in amount by the treatment are in brackets. "Unchanged" indicates that the sample still contained cordierite, corundum and sapphirine.

Once the lower temperature limit of mullite formation had been determined, the reversibility of the four-phase reaction could be demonstrated. For example, once mullite had been formed at 1405° in the sample containing 1.5% iron oxide, the mullite-containing mixture was reheated ~10° C below the critical temperature (in this instance, 1397° C), and it was found that the mullite disappeared in 168 h.

4. Discussion

Relative to their component oxides, the free energies of formation of the ternary compounds, e.g. sapphirine and cordierite, are likely to be only slightly negative with respect to those of the binary compounds, e.g. mullite, spinel, etc. In many systems, a consistent pattern of free energies obtains which persists over the range of temperatures from 0 K to the solidus. In this system, however, several changes occur in relatively rapid sequence as the melting point is approached. The quality of the presently available thermodynamic data do not permit a quantitative treatment of these changes but a qualitative rationale is as follows. The structures of cordierite and sapphirine are such that as their melting points are approached, a considerable excess positive contribution to the total entropy can be made by configurational and positional disordering of crystallochemically like atoms: Mg–Al and Al–Si. These additional contributions act in a manner so as to delay the onset of melting to as high a temperature as possible. Thus, the assemblages found to be stable at the liquidus (spinel, sapphirine and cordierite) and (sapphirine, mullite and cordierite) eventually commence melting at 1448 and 1454° C respectively, but this region of low-melting compositions is cut off and prevented from extending to higher-alumina compositions by the spinel–sapphirine–mullite region (solidus 1469° C) and especially, by the join spinel–mullite beyond which solidus temperatures rise to 1560° C. If, instead, the low-temperature assemblages shown in Fig. 1c were to remain stable up to their melting points, the solidus temperatures in a wide range of compositions extending toward Al_2O_3 could not possibly exceed the maximum melting temperature of cordierite itself (1465° C), and in all probability would be less than 1450° C. However, it is not possible to make the transition *directly* from the assemblages shown in Fig. 1c to the more refractory set of assemblages in Fig. 1a since to do so, the mullite–spinel join would have to cross three three-phase areas. Instead, the transition must be accomplished in one or more stages each of which obeys the phase rule. The experimentally-observed method by which this is achieved is shown in Fig. 1b; this "intermediate" state need exist stably only over a comparatively short range of temperatures.

The "subsolidus" phase relations depicted in Fig. 1a are compatible with the liquidus invariant points and are therefore, the correct phase distributions to show superimposed upon liquidus contours. Nevertheless, considerable care must be used in making predictions of the subsolidus phase equilibria from this diagram because this scheme of compatible phases is not an isothermal section through the system at any single temperature: it will be recalled that while some compositions have a solidus temperature as low as 1345° C, other of the solid-phase assemblages shown in Fig. 1a are not stable below 1460° C.

The correct procedure for predicting the stable phase distributions at temperature up to 1345° C is to use Fig. 1c as an isothermal section, making due allowance for the polymorphism of the $MgSiO_3$ and SiO_2 phases. Above 1345° C but below 1386° C, Fig. 1b must be combined with the liquidus data to produce an appropriate isothermal section while above 1460° C, the liquidus data must be combined with Fig. 1a.

An example of the application of these data arises in predicting the phase distribution of fired cordierite-containing aluminous ceramic bodies. Appropriate compositions are frequently observed to contain principally cordierite, mullite and corundum. From previously published data (either Fig. 1a or b), this phase combination would appear to be metastable. However, if firing temperatures do not exceed 1386° C the data in Fig. 1c are applicable, and this assemblage is seen to constitute a stable phase composition.

In its natural occurrences, sapphirine frequently occurs in intimate association with both cordierite and corundum. This occurrence is predicted from Fig. 1c, whereas from previously published data it would be concluded that cordierite—corundum assemblages would not be stable at 1 atm pressure.

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