JOURNAL OF MATERIALS SCIENCE 13 (1978) 671–674

Phase formation in the system MgO-Ga_2O_3-SiO_2

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Subsolidus phase equilibria in the MgO—Ga_2O_3—SiO_2 system were studied by sintering 18 compositions. A stable gallium analogue of sapphirine and a metastable mullite-like phase were prepared. Ga-sapphirine melts incongruently to $MgGa_2O_4$ and becomes liquid at 1490 ± 5° C. A diagram showing subsolidus phase compatibility at 1390° C is presented.

1. Introduction

In a previous paper [1], we described subsolidus compatibility relations in the system MgO—Al_2O_3—SiO_2. At that time we were uncertain about the exact compositions of two of the ternary phases, cordierite and sapphirine. We were hopeful that some of these problems might be resolved by studying a "model" system and, in searching for an appropriate model, we went back to look at compound formation and subsolidus equilibria in the MgO—Ga_2O_3—SiO_2 system. As the system has not previously been studied, we now briefly report our findings.

2. Experimental

Approximately 18 ternary compositions containing 20 to 70 mol% Ga_2O_3 were prepared from "AnalaR" $MgCO_3$, dried at 110° C, "Cera" Al_2O_3 and an electronic grade of Ga_2O_3 containing not less than 99.99% Ga_2O_3, both dried at 900° C. The weighed batches were moistened with alcohol, ground by hand in agate mortars, dried, and fired at 1100 to 1200° C in platinum crucibles. It was generally necessary to refire aliquots, contained in platinum foil envelopes, at progressively higher temperatures until complete reaction was obtained. Most of the firings were done in muffle furnaces in which temperatures were controlled and measured to ± 10 to 15° C. Accurate control of temperatures was not generally important; where it was, a precision quench furnace was used and the accuracy of temperature control and measurement are stated. Table I lists the results obtained in experiments which yielded significant information.

Phases were identified optically using a petrographic microscope and by X-ray powder diffraction using a Guinier camera and CuK_{α_1} radiation. Powder X-ray data for the binary phases and for β-Ga_2O_3 were taken from the JPDF file.

3. Results and discussion

3.1. Ternary phase formation

We synthesized two hitherto unreported phases. From their X-ray powder patterns, shown in Tables II and III respectively, these appear to be the gallium analogues of sapphirine and mullite. We were unsuccessful in obtaining gallium cordierite at any temperatures between 1200 and 1450° C.

3.2. Gallium-sapphirine

Mixtures of MgO, Ga_2O_3 and SiO_2 (quartz) react rapidly to form sapphirine; typically in 12 to 24 h at 1420° C. Single-phase formation is aided by the fact that Ga-sapphirine has an appreciable range of composition, as shown in Fig. 1. The structure of Al-sapphirine has been determined by Moore [2] who finds that it has the composition $7MgO \cdot 9Al_2O_3 \cdot 3SiO_2$. We find that the 7:9:3 MgO:Ga_2O_3:SiO_2 ratio gives a homogeneous, single phase preparation. However, single-phase compositions also seem to extend in a triangular patch from approximately this point toward more gallia-rich compositions. The long sides of this triangle are bordered by two lines, one extending toward the MgO—Ga_2O_3 binary edge at 75 mol% Ga_2O_3 and the other by a line towards Ga_2O_3 itself. This patch also includes the 4:5:2 composition, which Foster [3] gives as the best esti-

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TABLE I Reactions of MgO, Ga_2O_3 and SiO_2

Composition (mol %)			Temperature (° C)	Time (h)	Phases present
MgO	Ga_2O_3	SiO_2			
34.73	42.83	22.44	1410	72	Sap + crist
40.97	40.15	18.88	1410	72	Sap + sp + en
44.75	42.95	12.30	1410	48	Sap + sp + en
33.41	50.06	16.53	1410	48	Sap
30.5	54.5	15.0	1410	48	Sap
32.0	54.5	13.5	1425	48	Sap
29.0	57.0	14.0	1425	48	Sap
31.0	57.0	12.0	1425	48	Sap
26.16	60.63	13.21	1425	48	Sap + β-Ga_2O_3
30.0	60.0	10.0	1425	48	Sap + sp + β-Ga_2O_3
29.0	52.0	19.0	1420	72	Sap + crist + mull(tr)
29.0	52.0	19.0	1425	168	Sap + crist
35.0	52.0	13.0	1420	72	Sap + sp
31.75	20.64	47.62	1360	48	Sap + crist + en
54.76	23.02	22.22	1370	72	En + fo + sp
21.0	27.0	52.0	1370	72	Sap + crist
16.0	48.0	36.0	1370	72	Sap + crist + β-Ga_2O_3 + mull (tr)
16.0	48.0	36.0	1370	168	Sap + crist + β-Ga_2O_3
–	60	40	1400	168	Crist + β-Ga_2O_3
36.36	45.45(4:5:2)	18.19	1410	72	Sap
			1472	24	Sap
			1481	24	Sap
			1487	24	Sap
			1493	24	Sp + liquid
22.03	22.03(2:2:5)	55.93	1370	48	Sap + en + crist
			1385	24	Sap + en + crist
			1405	24	Sap + crist + liquid
			1427	24	Crist + liquid

Abbreviations: Sap = sapphirine, crist = cristobalite (SiO_2), sp = spinel ($MgGa_2O_4$), en = enstatite or protoenstatite ($MgSiO_3$), fo = forsterite (Mg_2SiO_4), mull = mullite, (tr) = trace.

mate, from quenching data, of the composition of Al-sapphirine. Semi-quantitative diffraction experiments made using weighed mixtures of various phases show that as little as 1 to 2% spinel or β–Ga_2O_3 can be detected in the presence of sapphirine. We are convinced, therefore, that the ternary "patch" of single-phase sapphirine compositions is real and that its shape at 1420° C is known with reasonable accuracy which, in this instance is ± 1 mol %.

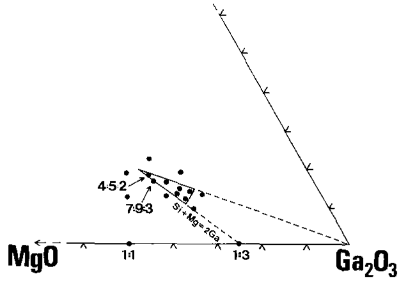

Figure 1 The region of homogeneity of the sapphirine phase in the system MgO–Ga_2O_3–SiO_2 at 1420° C.

Sapphirine solid solution extending towards 75 mol % Ga_2O_3 or "$MgO \cdot 3Ga_2O_3$" suggests that the substitution ($Mg^{2+} + Si^{4+}$) = $2Ga^{3+}$ is occurring. Schreyer and Abraham [4] have reported the occurrence of peraluminous sapphirines in nature and suggest that the end-member of this series is $MgO \cdot 3Al_2O_3$. Gallium sapphirines thus show an analagous trend. Solid solution towards the R_2O_3 end-member has not hitherto been suggested, but it is of course known that the spinels – $MgAl_2O_4$ and $MgGa_2O_4$ – form solid solutions with Al_2O_3 or Ga_2O_3, respectively [5, 6]. Sapphirine has a decided structural similarity to spinel, and it seems reasonable that solid solution between Ga-sapphirine and Ga_2O_3 should also be possible.

TABLE II Crystallographic and X-ray powder data* for Ga-sapphirine

$d_{(\text{obs.})}$ (Å)	I/I_0	$d_{(\text{calc.})}$ (Å)	hkl
7.94	6	7.943	1 1 0
7.37	5	7.378	0 2 0
4.72	4	4.713	2 0 0
4.16	15	4.162	$\bar{1}$ 2 2
3.972	5	3.972	2 2 0
3.687	8	3.689	0 4 0
3.433	5	3.435	1 4 0
3.364	5	3.365	$\bar{3}$ 2 2
3.174	7	3.176	0 3 2
3.075	62	3.073	3 1 0
2.978	5	2.977	$\bar{1}$ 4 2
2.920	40	2.921	1 2 2
2.845	12	2.845	$\bar{4}$ 1 2
2.763	7	2.767	2 3 1
2.751	5	2.754	$\bar{4}$ 0 3
2.722	6	2.724	0 1 3
2.672	8	2.675	$\bar{4}$ 1 1
2.639	30	2.640	$\bar{3}$ 4 2
2.554	7	2.553	$\bar{4}$ 2 1
2.515	100	2.520	$\bar{2}$ 0 4
		2.514	$\bar{2}$ 5 2
2.410	35	2.409	1 4 2
		2.407	0 5 2
2.366	5	2.369	$\bar{4}$ 1 4
2.309	8	2.308	$\bar{1}$ 1 4
2.285	5	2.283	$\bar{4}$ 2 4
2.209	5	2.210	$\bar{1}$ 6 2
2.181	8	2.180	2 6 0
2.132	12	2.132	$\bar{5}$ 1 4
2.079	55	2.079	0 0 4
2.070	84	2.068	$\bar{4}$ 5 2
2.003	5		
1.947	10		
1.875	5		
1.808	7		
1.756	5		
1.733	5		
1.704	5		
1.666	5		
1.593	50		
1.583	20		
1.574	5		
1.548	5		
1.476	45		
1.457	65		
1.454	20		
1.451	10		

Crystallography: monoclinic, $P2_1/a$; $a = 11.598 \pm 0.005$ Å, $b = 14.757 \pm 0.006$ Å, $c = 10.233 \pm 0.005$ Å, $\beta = 125.64°$

*α-Al_2O_3 was used as an internal standard, $a = 4.758$ Å, $c = 12.991$ Å

TABLE III Powder data for mullite-like phase

d (Å)	I	d (Å)	I
5.40	w	2.430	vw
2.700	w	2.210	w
2.540	m	1.600	w

The powder X-ray data are shown for a 4:5:2 sapphirine, but the X-ray d-spacings remain virtually unaffected by solid solution. The 4:5:2 Ga-sapphirine melts incongruently to Ga-spinel at 1490 ± 5° C. We do not know the composition accurately of the last trace of sapphirine which is in equilibrium with liquid.

3.3. Gallium-mullite

In a study of the system Ga_2O_3–SiO_2, gallium-mullite was not encountered [7]. In the present study, we have sintered both Ga-mullite and Ga-sillimanite (Ga_2SiO_5) compositions for several weeks. No phases other than β-Ga_2O_3 and cristobalite were found. Addition of MgO, however, produces a mullite-like phase within a few days. It is undoubtedly metastable, as it disappears in experiments at the same temperatures but of longer duration. Table III shows some typical results. Since all preparations giving Ga-mullite contained several phases, the powder data for Ga-mullite shown in Table II have been found by subtraction of the powder lines due to "impurity" phases. Each of these could be obtained pure and shown to have a definite, well-characterized powder pattern and the positions and intensities of the remaining reflections not accounted for by these subtractions are strongly suggestive of a mullite-like phase. We considered also the possibility that the phase was a gallium-sillimanite (Ga_2SiO_5) but a comparison of relevant powder patterns did not provide any support for this hypothesis, nor was the yield of the metastable phase increased by going from the 3:2 to the 1:1 ratio of $Ga_2O_3:SiO_2$. The role of Mg is clearly crucial in developing the mullite phase: however, we do not know if this is a kinetic phenomenon or if Mg actually participates in the structure of the mullite phase. It may be noted that Al-mullite contains little if any Mg.

3.4. Gallium-cordierite

Efforts to make gallium-cordierite were unsuccessful. We also attempted to make gallium-containing cordierites by replacing Al progressively by Ga. The general formula of the solid solutions would be $2MgO \cdot 2(Al_{1-x}Ga_x)_2O_3 \cdot 5SiO_2$. At $x = 0.1$, an apparently single phase preparation was obtained by sintering at 1350°, but at $x = 0.25$, a gallium-rich sapphirine appeared and we were unable to produce a single-phase preparation.

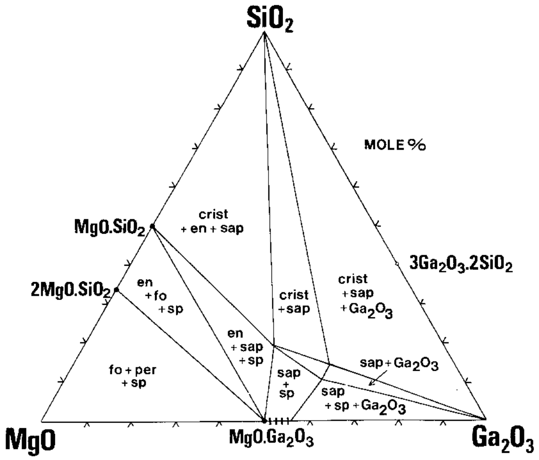

Figure 2 Composite isothermal section of the ternary system $MgO–Ga_2O_3–SiO_2$ at 1390° C.

3.5. Ternary phase relationships

From data obtained at temperatures between 1360 and 1425° C we have constructed a ternary diagram (Fig. 2) showing compatible phase assemblages. Since the solid-phase compatibilities do not change in this temperature range, it can be regarded as an isothermal section at approximately 1390° C. The gallium-mullite compositions is shown for reference since it is not believed to exist stably in this temperature range. The 2:2:5 composition commences melting at 1392 ± 7° C. This point, believed to be a eutectic, is probably the minimum melting point in the ternary system.

Acknowledgement

This investigation was supported by the Department of Industry, National Physical Laboratory, Agreement No. 1116/03.

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Received 10 June and accepted 22 July 1977.