

SYNTHESIS AND PROPERTIES OF GALLIUM-  
BEARING CORDIERITE,  
 $Mg_2(Al_{4-x}Ga_xSi_5O_{18})$

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ABSTRACT

On the join  $Mg_2Al_4Si_5O_{18}$ —“ $Mg_2Ga_4Si_5O_{18}$ ” Ga-bearing cordierites could be synthesized from glasses at 1 atm as well as hydrothermally. The limit of stable solid solubility lies at about 12 mole percent of the theoretical Ga-end member at 750°C/3kb, 900°C/1kb 1000°C/1kb. The most Ga-rich cordierite,  $Mg_2(Al_{3.2}Ga_{0.8}Si_5O_{18})$ , synthesized in the dry system at 1050°C/15 hrs was metastable. Ga-cordierites prepared at about 1000°C/1atm are hexagonal. Lattice constants and mean refractive index increase with increasing substitution of Ga for Al. At 1350°C a hexagonal cordierite of the composition  $Mg_2(Al_{3.6}Ga_{0.4}Si_5O_{18})$  could be transformed into a “low”-cordierite. The structural distortion of hydrothermally synthesized samples increased with raising Ga-contents.

INTRODUCTION

In 1950 J. R. Goldsmith succeeded in synthesizing the gallium analogues of the feldspars albite and orthoclase,  $NaGaSi_3O_8$  and  $KGaSi_3O_8$ . Pure gallium anorthite,  $CaGa_2Si_2O_8$ , first synthesized by Trömel (*cf.* Eitel *et al.*, 1930), was found to be a metastable compound, but partly substituted Ga-anorthites, *e.g.*  $CaAlGaSi_2O_8$ , could be obtained as stable phases (Goldsmith, 1950). Therefore, it was assumed that a substitution of aluminum by gallium might be possible also within the structure of cordierite,  $Mg_2(Al_4Si_5O_{18})$ , which had first been classified as a framework silicate along with feldspars by Zoltai (1960). The justification of this classification was later confirmed by the results of structure refinements by Gibbs (1966) and Meagher (1967). On the other hand, Hafner and Schreyer (unpublished results, quoted by Schreyer 1964) failed to synthesize pure Ga-cordierite in the system  $MgO$ - $Ga_2O_3$ - $SiO_2$  (- $H_2O$ ). However, during the course of a systematic experimental investigation on substitutions in the structure of cordierite it seemed necessary to know, whether or not aluminum could be replaced at least in part by gallium. If so, the extent of solid solubility along the pseudobinary section  $Mg_2Al_4Si_5O_{18}$ —“ $Mg_2Ga_4Si_5O_{18}$ ” of the quaternary system  $MgO$ - $Al_2O_3$ - $Ga_2O_3$ - $SiO_2$  was to be determined.

EXPERIMENTAL METHODS

Finely powdered, homogeneous glasses of the composition  $2MgO \cdot (2-x)Al_2O_3 \cdot xGa_2O_3 \cdot 5SiO_2$  served as starting materials for crystallisation experiments in the dry system as well as under hydrothermal conditions. These glasses, the composition and refractive index of which is given in Table 1, were prepared at 1550°C by fusing the oxides  $MgO$  (reagent grade; Merck, Darmstadt),  $Al_2O_3$  (from 99.99 percent Al metal; Merck, Darmstadt),

Table 1. Composition And Refractive Index Of Glasses  
Serving As Starting Materials For  
Experiments On The Join  $Mg_2Al_4Si_5O_{18}$  - " $Mg_2Ga_4Si_5O_{18}$ "

Glass No.	mole % " $Mg_2Ga_4Si_5O_{18}$ "	n
G2	0	1.555
CGA5	5	1.558
CGA1	10	1.562
CGA6	15	1.564
CGA2	20	1.568
CGA3	30	1.574
CGA4	40	1.581

$Ga_2O_3$  (99.99 percent; Schuchardt, München) and quartz (Dörentrupp). These oxides had previously been heated at 1350–1400°C until a constant weight was obtained. The techniques used in dry and hydrothermal crystallisation of the glasses, as well as in the identification of the products have been described elsewhere (Langer and Schreyer 1969; Povondra and Langer, 1970, in manuscript).

#### EXPERIMENTAL RESULTS

The conditions and results of *dry crystallisation* experiments performed at 1 atm with Ga-bearing cordierite glasses (*cf.* Table 1) are compiled in Table 2. It can be seen from the table that at appropriate conditions of annealing single phase Ga-bearing cordierites can be synthesized containing up to 20 mole percent of the theoretical gallium end member (runs 14 and 15), thus corresponding to a composition



On the other hand, runs 16 and 17 indicate that this 20 mole percent cordierite unmixes on continued heating at about 1050°C. From the results of hydrothermal experiments to be described below, it is evident that the limit of *stable* solid solubility at 1000°C lies at about 12 mole percent theoretical Ga- end member at 1kb. The same limit may hold at 1atm, because a strong pressure influences on solid solubility seems unlikely.

All the cordierites formed at 1atm exhibited a well defined powder X-ray diffraction diagram with sharp lines. No splitting or asymmetry of the critical interference at 29.5° 2 $\theta$  CuK $\alpha$  (*cf.* Miyashiro, 1957) could be detected. Therefore, these powder diagrams were indexed on the

Table 2. Conditions And Results Of Selected Crystallisation Experiments With Ga-bearing Cordierite Glasses (cf. Table 1.) At 1 ATM

Run No.	Starting material		Conditions		Phases obtained
	Glass No.	Mole % " $x\text{Ga}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ "	Temp. (°C)	Duration (hrs.)	
1	G2	0	1060	5	all cordierite
2			1050	110	all cordierite
3	CGA5	5	1060	5	all cordierite
4			1050	110	all cordierite
5	CGA1	10	900	140	cordierite + little stuffed high-quartz
6			1000	15	cordierite + stuffed high-quartz
7			1060	5	cordierite + trace stuffed high-quartz
8			1060	58	all cordierite
9			1050	110	all cordierite
10	CGA6	15	1060	5	cordierite + very little stuffed high-quartz
11			1050	110	all cordierite
12	CGA2	20	900	140	cordierite + little stuffed high-quartz + trace spinel
13			1000	15	cordierite + stuffed high-quartz
14			1060	5	all cordierite
15			1050	15	all cordierite
16			1060	60	cordierite + trace spinel? (only under the microscope; some very small crystals with high refract. ind. at grain borders of cordierite crystals)
17			1050	110	
18	CGA3	30	900	140	cordierite + stuffed high-quartz + trace spinel
19			1050	15	cordierite + trace high-quartz + very little spinel
20			1060	64	
21			1050	110	
22	CGA4	40	1060	5	cordierite + very little high-quartz + little spinel
23			1050	15	cordierite + little high-quartz + little spinel
24			1050	110	

basis of a hexagonal unit cell. The lattice constants thus obtained are plotted in *Figure 1* against composition of the samples which were prepared at 1050°C/ 110 hrs. (cf. Table 2). Sample 17 has been included, since only traces of other phases were observed under the microscope besides cordierite. In addition, the mean refractive indices of the samples are plotted in *Figure 1*. It can be seen from this figure that an increasing

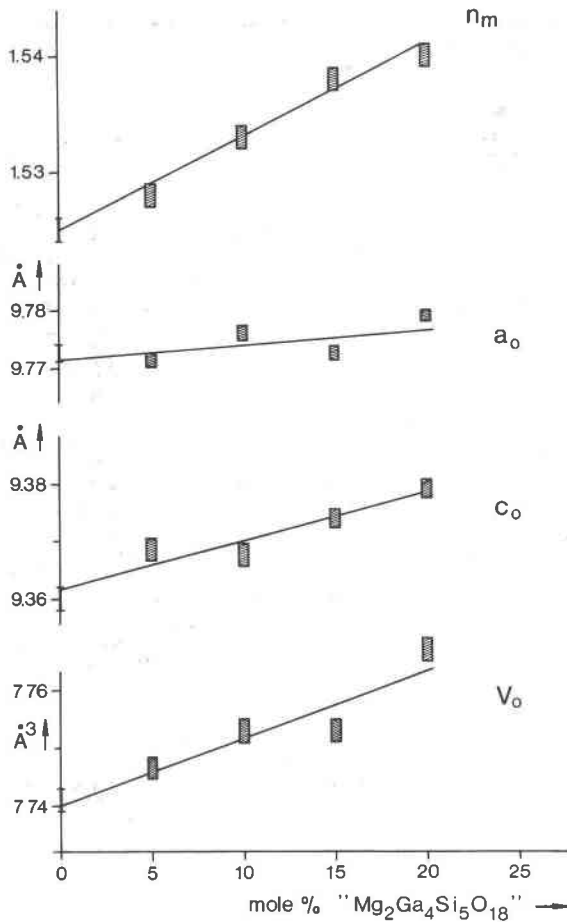


FIG. 1. Lattice constants and mean refractive index of hexagonal Ga-bearing cordierite as a function of composition. The samples were obtained through devitrification of glasses (cf. Table 1) at 1 atm and 1050°C/110 hrs. (cf. Table 2).

substitution of gallium for aluminum results in an increase of lattice constants and mean refractive index on account of the higher ionic radius and refractive energy of gallium as compared with aluminum. The unit cell volume of the cordierite structure is enlarged by 0.34 percent if 20 mole percent " $\text{Mg}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ " end member are taken up into solid solution. In Figure 2 the relative intensities of the peaks between 10 and 40°  $2\theta$   $\text{CuK}\alpha$  in the powder X-ray diagrams of cordierites obtained by crystallizing glasses (Table 1) at 1050°C/110 hrs are shown as a function of the Ga-contents of the samples. It is evident that the intensities of

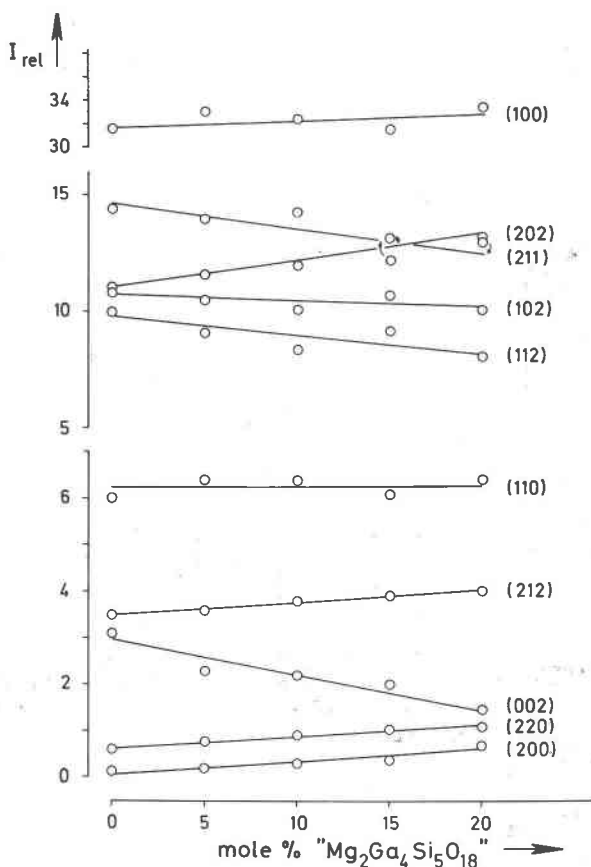


FIG. 2. Relative intensities of X-ray peaks between 10 and 40° 2θ CuKα in the powder diagram of Ga-bearing cordierites as a function of composition (same samples as in Fig. 1).

some reflections are changed appreciably with composition thus supporting the incorporation of gallium into the cordierite structure.

From the powder data of cordierite samples prepared at 1060°C/5 hrs and 1050°C/110 hrs (*cf.* Table 2) a calibration curve was constructed (Figure 3) in order to determine the Ga-contents of hydrothermally produced cordierites observing all the precautions mentioned by Povondra and Langer (1970, in manuscript). With the aid of this curve, the concentration of "Mg<sub>2</sub>Ga<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>" in cordierites from multiphase samples on the join Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>—"Mg<sub>2</sub>Ga<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>" can be determined with an accuracy of about ± 2 mole percent.

Schreyer and Schairer (1961), Schreyer and Yoder (1964), and Langer and Schreyer (1969) showed that hexagonal cordierites in the system

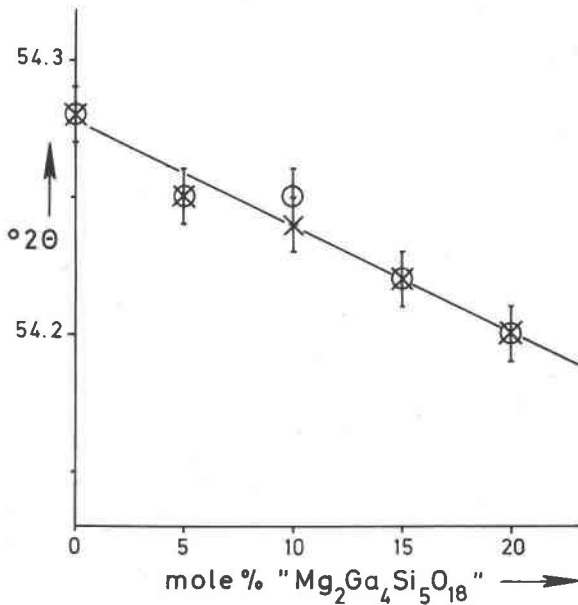


FIG. 3. Calibration curve for determination of gallium contents in cordierites along the join  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ —" $\text{Mg}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ ." The cordierite peak at about  $54.2^\circ 2\theta$   $\text{CuK}\alpha$  has been measured using  $\text{NaCl}$  (222) at  $56.53^\circ 2\theta$   $\text{CuK}\alpha$  as an internal standard. Samples were prepared by devitrification of glasses at 1 atm and  $1060^\circ\text{C}/5$  hrs (crosses) and  $1050^\circ\text{C}/110$  hrs (round dots).

$\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  formed through dry or hydrothermal devitrification of glasses in relatively short runs and at relatively low temperatures are metastable and transform on continued heating and at higher temperatures into stable orthorhombic cordierites. Similarly it might be supposed that the hexagonal Ga-cordierites described thus far are metastable considering the short run durations and low temperatures at which they were synthesized. If so, any subsolidus annealing of a hexagonal Ga-bearing cordierite at higher temperatures should result in a lower-symmetry distortion of the structure. Distortion should be indicated by an increase of the width index  $W1/3$  (Langer and Schreyer 1969) and, at relatively high degrees of orthorhombic distortion, by an increase of the distortion index  $\Delta$  (Miyashiro 1957).

In order to check the above assumption, a 10 mole percent Ga-cordierite (no.8, Table 2) has been heated at 1300 and  $1350^\circ\text{C}$  for various lengths of time. In the samples obtained, no additional phases could be detected, which would indicate unmixing or formation of melt at these

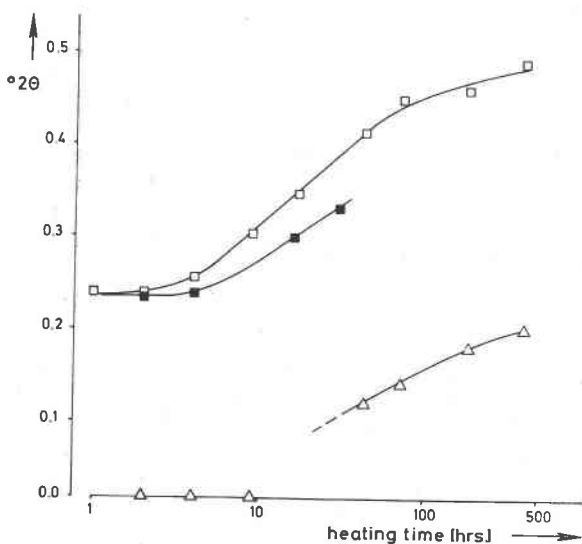


FIG. 4. Width index (boxes) and distortion index (triangles) of a 10 mole percent Ga-cordierite (sample 8, Table 2) as a function of heating time at 1300°C (filled symbols) and 1350°C (open symbols). The increase of the two properties during the heat treatment indicates increasing distortion of the structure.

temperatures. In *Figure 4* the width and distortion indices of the samples are plotted as a function of heating time. It can be seen from the diagram that these properties of Ga-bearing cordierites show a similar behavior as those observed for pure Al-cordierite,  $Mg_2Al_4Si_5O_{18}$ : structural distortion increases with heating time.

From the work of Meagher (1967), Fontaine (1969), and Langer and Schreyer (1969), it is evident that an increase of orthorhombic distortion is principally caused by ordering processes within the structure, though there is no direct and simple relation between degree of distortion and degree of order (Meagher and Gibbs 1966). Therefore, the increasing distortion of the initially hexagonal 10 mole percent Ga-cordierite upon heating at 1300 and 1350°C, as indicated by increasing width and distortion indices, confirms a process of ordering in general also for Ga-bearing cordierites. Because of their more complicated composition, these cordierites are likely to follow a more complicated ordering scheme than pure Al-cordierite,  $Mg_2Al_4Si_5O_{18}$ .

It is evident from the results of runs no. 5–8, 10 and 11, as well as 13 and 14 (Table 2) that the Ga-bearing cordierites are obtained through transformation of stuffed high-quartz derivatives formed as the first devitrification products of the glasses, similarly as in pure Al-cordierite. The position of X-ray peaks of these stuffed high-quartz phases in

the powder diagram of products 5, 6, 12, and 13 are not markedly shifted as compared with those of the pure 2:2:5 high-quartz phase. Through the incorporation of gallium, however, these high-quartz derivatives seem to be "stabilized" relative to pure 2:2:5 high-quartz, because they persisted for longer periods of heating at 1000°C (runs 6 and 13) than a pure 2:2:5 high-quartz derivative. (*cf.* Langer and Schreyer, 1969, Fig. 3)

At compositions far away from the limit of solid solubility (30 and 40 mole percent theoretical Ga-end member) a high-quartz phase different from the stuffed high-quartz derivatives just described, and a Ga-bearing spinel were observed as additional phases besides cordierite (runs 19–24, Table 2). The composition of this particular high-quartz must be close to  $\text{SiO}_2$  judging from peak position of (100)- and (101)-reflexions. In contrast to the stuffed high-quartzes, from which the cordierites are formed, this second type of high-quartz has relatively broad X-ray peaks. It is called "high-quartz" in Table 2. The composition of the spinel phase mentioned above, formed in samples with 20 mole percent " $\text{Mg}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ " or more is not known accurately. At 20 mole percent of the theoretical Ga-end member this phase (at most 1 percent by volume) has only been observed through microscopic investigation. At 30 and 40 mole percent end member characteristic spinel lines appeared in the powder X-ray diagrams. However, the peaks were very broad and sometimes asymmetric (runs 22 and 23), thus indicating very poor crystallisation and possibly inhomogeneities within this phase. The peak maxima of the interferences (220), (311), and (400) were found to lie at about 31.0, 36.3, and  $44.3^\circ 2\theta$   $\text{CuK}\alpha$ . Assuming linearity in the X-ray properties of spinel end members this may indicate a mean composition of approximately 50 mole percent  $\text{MgGa}_2\text{O}_4$  in the spinel solid solution.

In Table 3 the results and conditions of *hydrothermal crystallisation* experiments with Ga-cordierite glasses (Table 1) are compiled. Stable solid solubility seems to extend up to about 12 mole percent " $\text{Mg}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ " at 750°C/3 kbar, 900°C/1 kbar, and 1000°C/1 kbar. Higher Ga-contents found in cordierites obtained from glasses CGA2 and CGA3 besides low-quartz and Ga-bearing spinel are presumably metastable, because the cordierites obtained at 1000°C are found to be poorer in gallium than those formed at 900°C (runs 13 and 14). The spinel formed in addition to cordierite and low-quartz outside the range of stable solid solubility is well crystallized compared with that formed in the dry system. Its composition is about  $\text{Mg}(\text{Al}_{1.2}\text{Ga}_{0.8})\text{O}_4$ .

As is to be expected (*cf.* Schreyer and Yoder 1964), the orthorhombic distortion of the cordierites synthesized increases with the temperature of synthesis. However, it is of interest to compare cordierites of different Ga-contents synthesized at identical conditions of pressure and temperature: The orthorhombic distortion of the structure is found to be higher in more Ga-rich cordierites (*cf.* Table 3). From this it is evident that substitutions in the framework of the cordierite structure may influence the degree of distortion. Another example for such behavior of cordierites had been found as a consequence of substituting aluminum by the smaller beryllium (Povondra and Langer, in manuscript), where the degree of distortion was found to decrease as compared to pure  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ .



Table 3. Conditions And results of some hydrothermal runs with Ga-bearing Cordierite Glasses (cf. Table 1.). The Contents of " $\text{Mg}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ " In Cordierite has been Determined Using The Calibration Curve Shown In Figure 3.

Run No.	Starting material Glass	mole % " $\text{Mg}_2\text{Ga}_4\text{Si}_5\text{O}_{18}$ "	Conditions			Phases obtained	mole % Ga-end member in cord.	Distortion of cord.		mole % $\text{MgGa}_2\text{O}_4$ in spin
			Pressure (kb)	Temp. ( $^{\circ}\text{C}$ )	Duration (hrs.)			$\Delta$	$\mu/3$	
1	CG2	0	3	750	113	all cordierite		0.12	0.38	
2			1	900	91	all cordierite		0.14	0.44	
3			1	1000	46	all cordierite		0.16	0.44	
4	CGA5	5	3	750	84	all cordierite		0.16	0.44	
5			1	900	91	all cordierite		0.18	0.47	
6			1	1000	46	all cordierite		0.18	0.48	
7	CGA1	10	1	900	91	all cordierite		0.19	0.48	
8			1	1000	46	all cordierite		0.19	0.50	
9	CGA6	15	3	750	84	cordierite + very little low-quartz + very little spinel	12.5	0.17	0.47	
10			1	900	91	cordierite + very little low-quartz + very little spinel	12.5	0.21	0.50	
11			1	1000	46	cordierite + little low-quartz + little spinel	10	0.22	0.50	
12	CGA2	20	3	750	113	cordierite + little low-quartz + little spinel	15	0.16	0.47	ca. 40
13			1	900	91	cordierite + very little low-quartz + very little spinel	17	0.21	0.49	ca. 40
14			1	1000	46	cordierite + little low-quartz + little spinel	14	0.21	0.50	ca. 39
15	CGA3	30	3	750	84	cordierite + lots of low-quartz + lots of spinel	17.5			ca. 40
16	CGA4	40	3	750	113	very little cordierite + low-quartz + spinel (+ trace talc)				ca. 37

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