

INFRARED AND POWDER X-RAY DIFFRACTION  
STUDIES ON THE POLYMORPHISM OF CORDIERITE,  
 $Mg_2(Al_4Si_5O_{18})$

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ABSTRACT

Devitrification products of pure Mg-cordierite glass,  $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ , were obtained at 980°C and 1400°C after various lengths of time and studied by powder X-ray diffraction and infrared techniques. For a characterization of the early stages of the structural transition from high to "low" cordierite a newly defined width index ( $W_{1/3}$ ) was found to be a more sensitive X-ray parameter than the commonly used distortion index ( $\Delta$ ).

The glass, the metastable high-quartz structure, and the cordierite structure in general yield characteristic infrared spectra. Only the early stages of the high-to "low"-cordierite transition with width indices corresponding to  $\Delta$  values up to  $0.10^\circ$ - $0.17^\circ$  show concomitant variations of the spectra typical for short-range ordering processes, whereas the later stages can solely be defined by their X-ray properties and may be due to increasing long-range order. Therefore, the orthorhombic distortion of cordierite appears to depend on both short-range and long-range order and hence, the distortion index  $\Delta$  cannot be used as a measure of the degree of Si/Al order even in specimens of the same bulk composition.

INTRODUCTION

It has been shown in the past that order-disorder transitions in crystal-line substances are accompanied by characteristic changes of their infrared absorption spectra (*e.g.* Laves and Hafner, 1956; Hafner and Laves, 1957, 1961; Hafner 1961; Laves and Hafner 1962; Tarte and Collongues 1964; Tarte 1965). Laves and Hafner (1956) pointed out that Al/Si ordering processes in feldspars, in particular, cause stronger effects in the infrared spectra than in the powder X-ray diffraction patterns of these minerals. It was of interest, therefore, to use infrared techniques in the study of polymorphic transitions of cordierite in which Al/Si ordering processes are also known to play a dominant role. Miyashiro *et al.* (1955) initially proposed that Al and Si are disordered in the hexagonal and ordered in the orthorhombic form. In 1957 Miyashiro discovered various degrees of orthorhombic deviation from hexagonal symmetry which he characterized by the distortion index  $\Delta$ —this property probably representing a measure of the degree of Al/Si order. The stability relations of pure anhydrous Mg-cordierite,  $Mg_2(Al_4Si_5O_{18})$ , were investigated experimentally at 1 atmosphere by Schreyer and Schairer (1961a), who on the basis of their experiments, found supporting evidence for Al/Si ordering and introduced a nomenclature for the various structural states of cordierite depicted in Figure 1. A metastable phase of cordierite composition forming through devitrification of the glass was found by Schreyer and Schairer (1961b) to exhibit a stuffed

high-quartz structure. The refinement of the structure of orthorhombic "low"-cordierite by Gibbs (1966) revealed a framework completely ordered with regard to Al and Si. It was surprising, however, that Meagher and Gibbs (1966) found this same degree of ordering even in intermediate-state cordierite with  $\Delta = 0.12^\circ$  and 35 percent of ordering in high-cordierite with  $\Delta = 0.0^\circ$ . Although these data seem to indicate that the distortion index  $\Delta$  is not a reliable measure of the degree of Al/Si order, they do prove that the hexagonal symmetry of high cordierite is caused by at least partial disorder of Al and Si.

For these reasons, it was hoped that infrared measurements might provide independent data useful for characterizing cordierite polymorphs especially those with low  $\Delta$  values which cannot be readily measured (Schreyer and Yoder 1964). Based on the earlier experiences with infrared spectroscopy quoted in the beginning, such data were also ex-

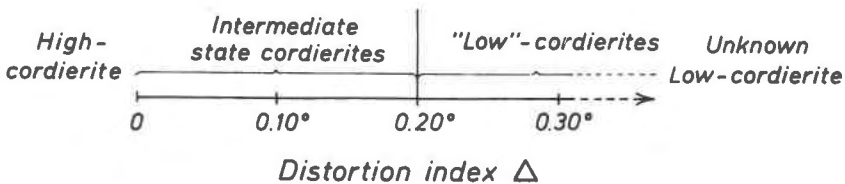


FIG. 1. Relations between the structural states of cordierite as a function of the distortion index  $\Delta$  using the nomenclature proposed by Schreyer and Schairer (1961a).

pected to contribute independent evidence for ordering processes in general connected with the orthorhombic distortion of the cordierite structure.

Infrared spectra of cordierites have previously been reported by Matossi and Krüger (1936), Bokii and Plusnina (1958), Plusnina and Bokii (1959), Moenke (1962), and Newton (1966). However, no application has been made to the ordering problem.

Additional infrared work by Sugiura (1959), Schreyer and Yoder (1964), and Farrel and Newnham (1967) was aimed at clarifying the role of water in the cordierite structure.

#### EXPERIMENTAL METHODS

In the present study anhydrous samples of the bulk composition  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  were investigated exclusively. The starting material was a homogeneous glass prepared at  $1550^\circ\text{C}$  by fusing oxides of high purity:

MgO	4N	Koch and Light,	Colnbrook, England;	batch No.25004
Al <sub>2</sub> O <sub>3</sub>	6N	Koch and Light,	Colnbrook, England;	batch No.28805
SiO <sub>2</sub>	6N	Koch and Light,	Colnbrook, England;	batch No.32200

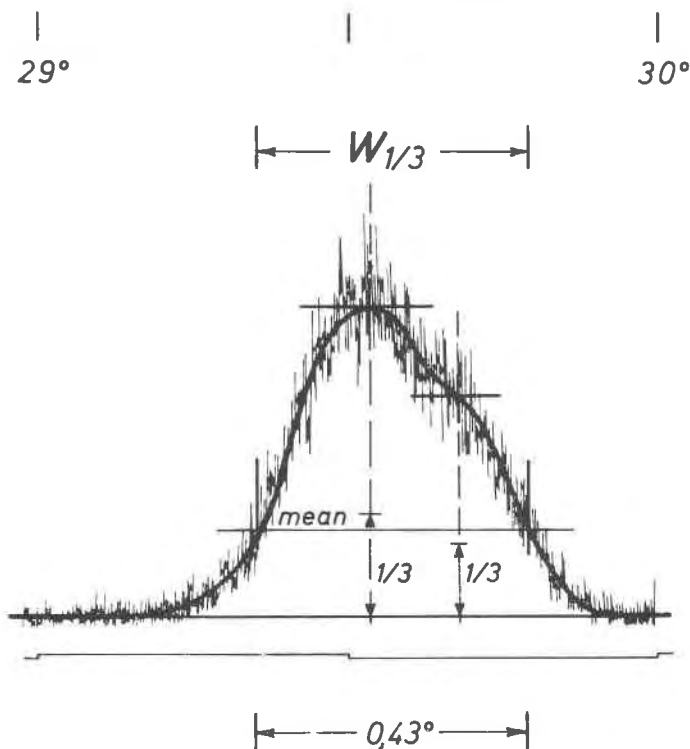


FIG. 2. Definition and procedure of measuring the width index  $W_{1/3}$  in a powder X-ray diffraction chart of cordierite run through the critical region of  $2\theta=29^\circ$ – $30^\circ$  for  $\text{CuK}\alpha$  radiation using the following setting of a Philips X-ray diffraction unit: 50 kV, 30 mA, Ni filter, slits  $1/6^\circ$ – $0.1$ – $1/6^\circ$ , scanning rate  $1/8^\circ/\text{min}$ , ratemeter adjustment 400/0.5/0; chart speed 1200 mm/hr.

These oxides had previously been ignited at  $1500^\circ\text{C}$  for 6 hours. The techniques employed were the same as those described by Schreyer and Schairer (1961a). The analyzed iron contamination calculated as  $\text{Fe}_2\text{O}_3$  was 0.15 wt %. The refractive index of the glass was found to be 1.555. Finely powdered samples of this glass were heated and thus devitrified at  $980^\circ$  for various lengths of time. Other samples preheated at  $980^\circ\text{C}$  for 305 hours were subsequently ignited at  $1400^\circ\text{C}$  up to 167 hours.

The crystalline products obtained were studied optically and by powder X-ray diffraction methods. Lattice constants of the high-quartz solid solution ( $\text{quartz}_{\text{ss}}$ ) as well as of high cordierite were determined from the diffraction patterns according to the method described by Donnay *et al.* (1959) using Si as an internal standard. The structural states of the cordierites synthesized were identified by two methods: (1) by measuring the distortion index  $\Delta$  in the usual manner, and (2) by measuring the width of the peak, or peak triplet, respectively, located near  $29.5^\circ 2\theta$  for  $\text{CuK}\alpha$  radiation at one third of its total intensity in the diffraction patterns run on samples of invariable quantity as demonstrated in Figure 2. This property will be called *width index* ( $W_{1/3}$ ) throughout this paper.

The infrared spectra were recorded by means of a double beam prismgrating spectro-

photometer, type IR 9, from Beckman Instruments using the CsJ-prism equipment in the range 250–700  $\text{cm}^{-1}$  and the KBr-prism equipment in the range 400–4000  $\text{cm}^{-1}$ . The instrument was operated with a slit program resulting in a spectral slit width of 1  $\text{cm}^{-1}$ . As all bands of the spectra recorded showed half intensity widths of 10  $\text{cm}^{-1}$  or higher, slit errors are equal to or less than 1 percent (Ramsey 1952). The scanning rate was 20  $\text{cm}^{-1}/\text{min}$ . The spectra were recorded in absorbance as well as in transmittance.

The samples for infrared work were prepared following the KBr disk technique. In order to avoid water bands in the spectra, the samples mixed with KBr (Uvasol, Merck) were dried under vacuum at 130°C over  $\text{P}_2\text{O}_5$  and subsequently pelletized, again under vacuum, using a pressure of 200  $\text{kg}/\text{cm}^2$ . The sample concentration was 0.18 percent (w./w.), the thickness of the pellets  $1.255 \pm 0.005$  mm. The reference beam was directed through a pure KBr pellet prepared in the same manner.

### RESULTS OF POWDER X-RAY STUDIES

In agreement with the results of Schreyer and Schairer (1961b) the first crystalline phase forming upon devitrification of the glass at 980°C was found to be a metastable quartz solid solution with cordierite composition. This phase, which is a stuffed derivative of high-quartz similar to high-eucryptite,  $\text{LiAlSi}_4\text{O}_{10}$ , (Winkler 1948, 1953), disappears again upon further heating at 980°C through a reconstructive transformation into high-cordierite. The upper portion of Figure 3 shows the relative proportions of the high-quartz phase and high-cordierite as a function of heating time by means of the intensity variations of their strongest powder X-ray reflections. After about 40 minutes the maximum amount of high-quartz<sub>ss</sub> is present, whereas practically no high-cordierite has formed as yet. After about 2 hours all this high-quartz has been transformed into high cordierite. As shown in the lower portion of Figure 3, the lattice parameters of both phases remain constant over the whole period of their existence. This appears to indicate that both the primary crystallization of the high-quartz<sub>ss</sub> as well as its transformation into high-cordierite are isochemical processes. No other crystalline phases than the two described could be detected.

Although high-cordierite is a metastable phase itself at 980°C (Schreyer and Schairer 1961a), no deviations from hexagonal symmetry could be detected in the cordierite phase even after heating for 305 hours. Only its width index  $W_{1/3}$  was found to decrease slightly with prolonged heating (left side of Fig. 4) probably due to grain growth.

In order to transform high-cordierite into "low"-cordierite a temperature of 1400°C was employed for various lengths of time. The results are also plotted in Figure 4 (right portion). The increase of the distortion index  $\Delta$  with duration of heating (lower curve) corresponds, in essence, to the earlier findings of Schreyer and Schairer (1961a, Fig. 16), but the measurements of  $\Delta$  remain unsatisfactory for low values. On the other hand, determination of the newly defined width index  $W_{1/3}$  (upper curve)

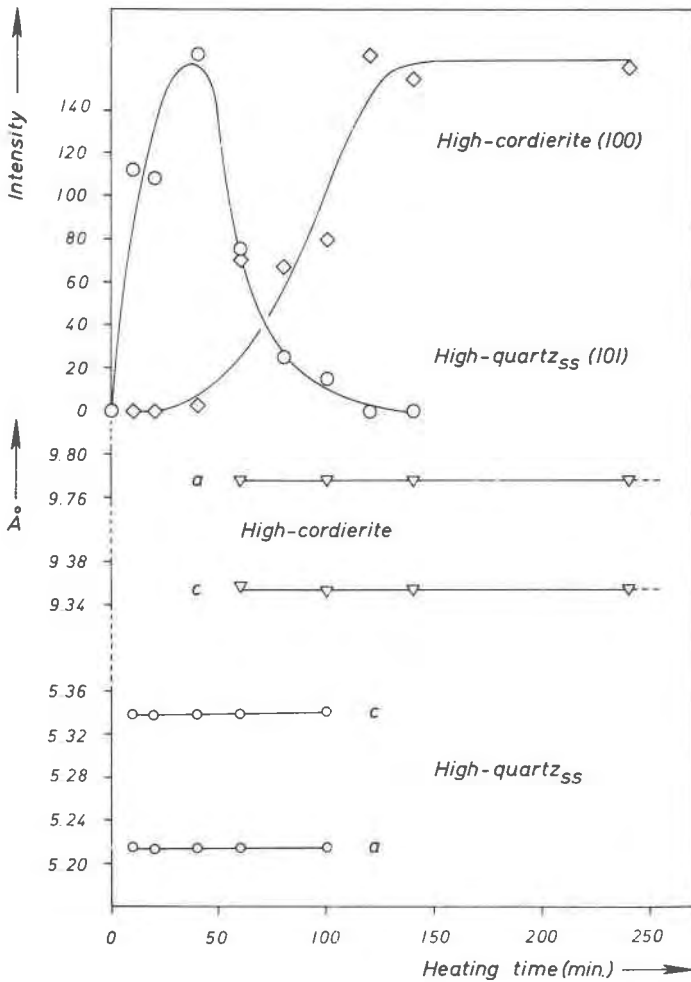


Fig. 3. Powder X-ray diffraction data of devitrification products of Mg-cordierite glass obtained at 980°C as a function of heating time. The relative intensities of the high-cordierite (100) and high-quartz<sub>SS</sub> (101) peaks have not been scaled.

yielded considerably more information: Whereas  $\Delta$  has remained zero within the first hour of heating, the width index has already attained about 15 percent of its total increase observed after 167 hours. Since the continued effect of grain growth would tend to lower  $W_{1/8}$ , it is concluded that its measured increase is due to incipient deviation of the cordierite structure from hexagonal symmetry. Thus the width index may be considered a more reliable parameter for the structural states of intermediate

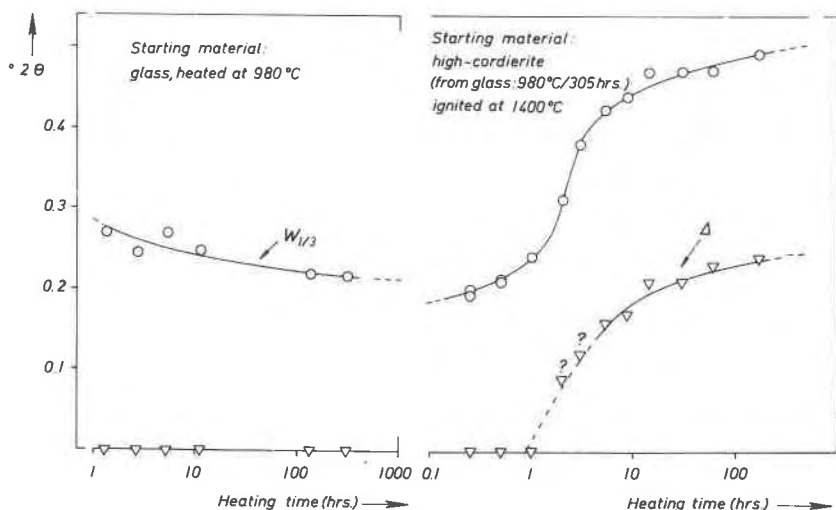


Fig. 4. Width index ( $W_{1/3}$ ) and distortion index ( $\Delta$ ) of Mg-cordierite samples as a function of heating time at two different temperatures.

cordierites than the distortion index. Unfortunately, however, this width index being a relative parameter can only be used if compared with that of a reference sample of identical composition and of known thermal history.

#### RESULTS OF INFRARED INVESTIGATIONS

Of all the samples characterized by powder X-ray diffraction methods in the previous section, infrared spectra were recorded. Those spectra critical for distinguishing different stages of the thermal history are reproduced in Figures 5 and 6, spectra I–X. The measured wave numbers of all the observed bands in six of these spectra are listed in Table 1.

The spectrum of cordierite glass (Fig. 5, I) already shows three pronounced broad bands designated *A*, *E*, and *F*, which reappear, characteristically modified, in all subsequent spectra of the crystallized material. The high-quartz spectrum (Fig. 5, II) contains these bands slightly shifted to higher wave numbers and with stronger intensities; in addition, a new band, *D*, appears for the first time.

One characteristic feature of the high-cordierite spectra (Fig. 5, III–V and Fig. 6, VI) as compared with spectra I and II is the appearance of an additional band, *B*. Moreover the relative intensities of bands *E* and *F* are reversed in comparison to the glass spectrum, and band *F* is again shifted to still higher wave numbers; band *A* splits up into three sub-bands and two small shoulders show up in the range *C*. in spectra III

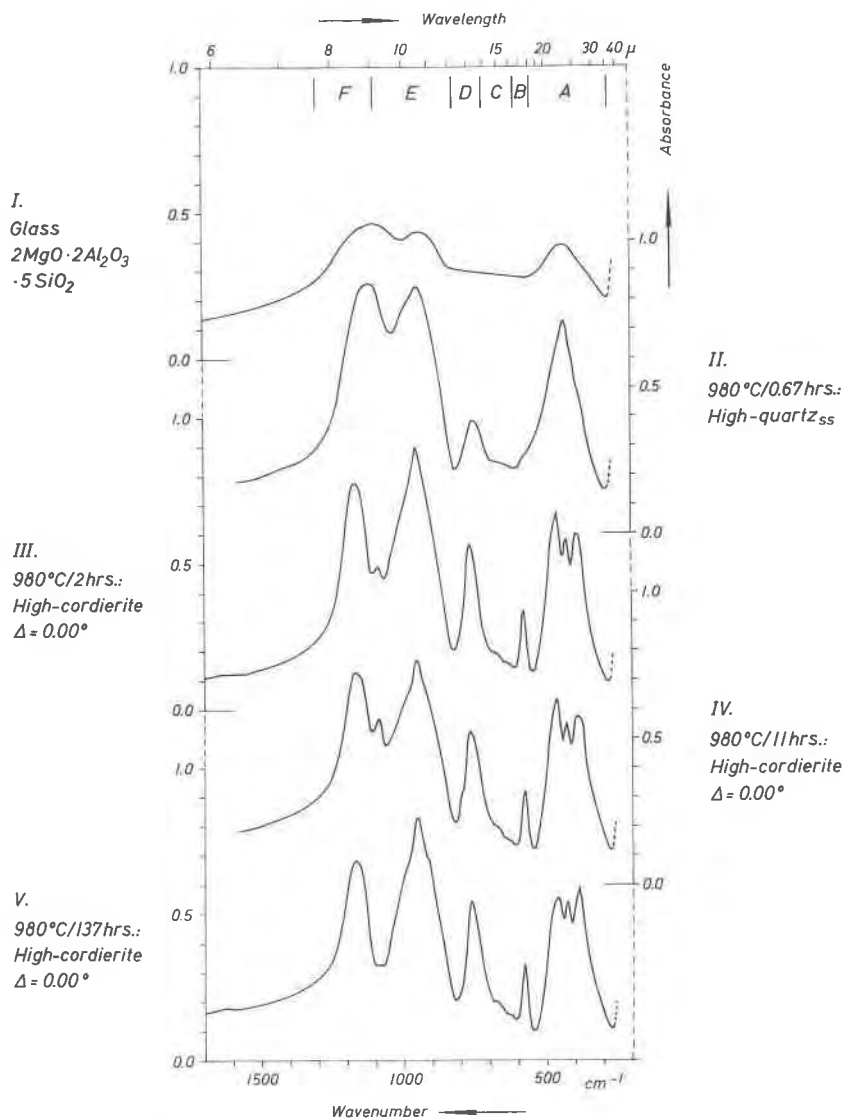


FIG. 5. Infrared absorption spectra of glass and various devitrification products of Mg-cordierite composition. The regions of the spectra discussed in the text are designated by the letters *A-F* in the uppermost portion of the figure. The absorbance scales applying to spectra *I-V* are shown intermittently on both sides of the diagram.

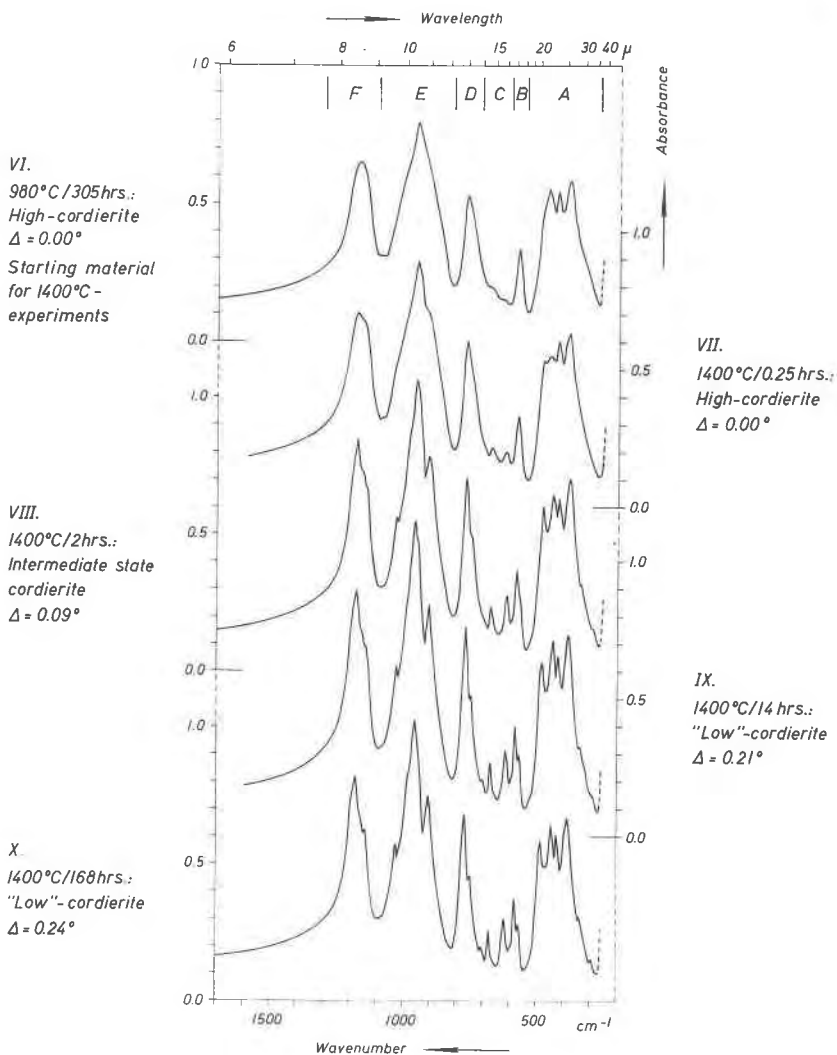


FIG. 6. Infrared absorption spectra of various Mg-cordierite polymorphs. Designation of these spectra VI-X as in Fig. 5.

and IV of the high-cordierite sequence a band develops between *E* and *F* which, however, almost disappears again, after continued heating of the sample (spectra V and VI).

The structural transition from high- towards "low"-cordierite incited through heating the sample at 1400°C is characterized in the infrared



TABLE 1. POSITION OF ABSORPTION BAND MAXIMA IN THE INFRARED SPECTRA OF Mg-CORDIERITE GLASS, 2 MgO·2Al<sub>2</sub>O·5SiO<sub>2</sub>, HIGH-QUARTZ SOLID SOLUTION, AND VARIOUS CORDIERITE POLYMORPHS OBTAINED FROM THIS GLASS (cf. FIGS. 5 AND 6)

Band system	I	II	III	VI	VIII	X	Single bands		
	Glass	High-quartz <sub>ss</sub> 980°C/0.67 hrs	High-cordie- rite 980°C/2 hrs	High-cordie- rite 980°C/305 hrs	Intermediate- state cordierite 1400°C/2 hrs	"Low-cordierite" 1400°C/167 hrs			
A	440b	432b				297	295	A <sub>1</sub>	
						344	340	A <sub>2</sub>	
			385	387	386	386	386	A <sub>3</sub>	
			428	429	426	426	425	A <sub>4</sub>	
					463	463	449	446	A <sub>5</sub>
							486	486	A <sub>6</sub>
B			576	578	569s	568	B <sub>1</sub>		
					582	582	598s, vw	B <sub>2</sub>	
C		650s, b	630s	628	621	620	C <sub>1</sub>		
			680s	677	679	~655s, vw	C <sub>2</sub>		
					705s, vw	708 vw	C <sub>3</sub>		
D		750	769	768	752	751	D <sub>1</sub>		
					771	771	D <sub>2</sub>		
E	935b	950b	956	957		~830s, vw	E <sub>1</sub>		
						911	908	E <sub>2</sub>	
						958	958		
							~975s		
							~1010s		
			1029	1030	E <sub>3</sub>				
			1090	1090	1080s, vw				
F	1100b	1115b	1175	1175	1145s	1148	F <sub>1</sub>		
					~1165s	~1160s	F <sub>2</sub>		
				1182	1180				

s=shoulder, vw=very weak, b=broad

spectra (Fig. 6, VII-X) by increasingly pronounced splitting of the bands A, B, D, E, and F, and an increasing intensity of bands C. These changes of the spectra take place mainly within the first 14 hours of heating (spectra VII-IX), that is concomitantly with the main increase of the distortion and width indices (cf. Fig. 4).

Careful measurements of the infrared spectra indicate that in the course of the high-low transition of cordierite at 1400°C the positions of the band maxima are not changed appreciably (Table 1 and Fig. 7). This is in contrast to the results of Hafner and Laves (1957) obtained on feldspars.

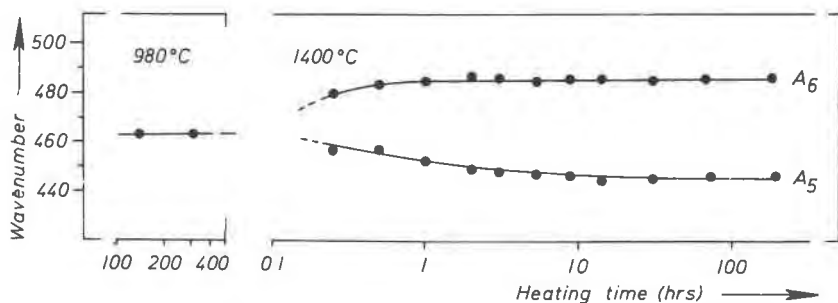


FIG. 7. Wavenumber of absorption band  $A_5$ - $A_6$  (cf. Figs. 6 and 8) as a function of heating time at two different temperatures.

In order to obtain a closer insight into the process of band splitting, the band systems of four critical spectra were analyzed by means of a Dupont curve resolver. As an example the analysis of band system  $A$  in spectra VI and X is shown in Figure 8. The main result of this work is

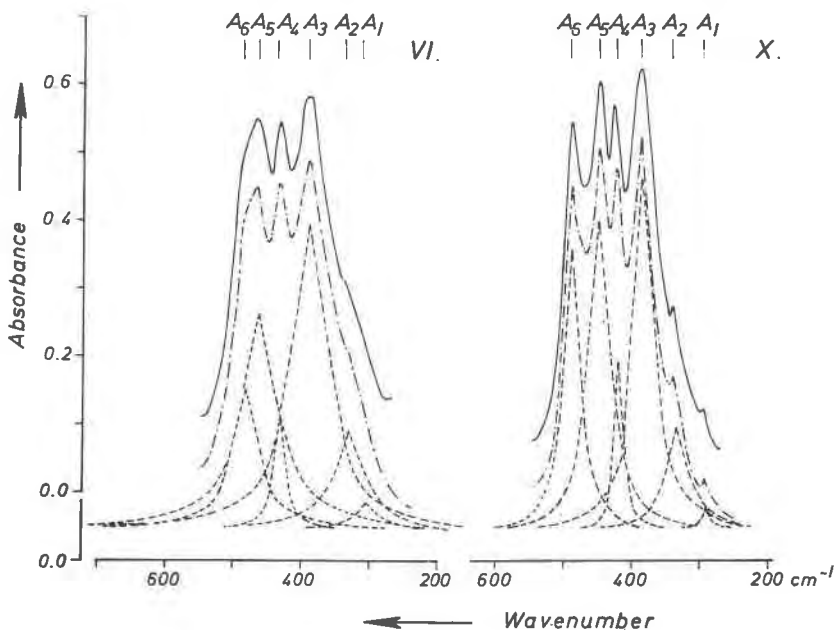


FIG. 8. Band analyses of infrared absorption band system  $A$  in the spectra VI and X (cf. Fig. 6): Solid curves represent the observed spectra, dashed curves the separate bands as resolved through analysis, and dot dashed curves the synthetic spectra obtained by summation of these separate bands. For better comparison of the synthetic and observed spectra the origin of the ordinate applying to the observed spectra has been shifted upscale by 0.1 units.

that all the bands appearing as separate peaks in the spectrum of "low"-cordierite (spectrum X) are also present in the spectra of intermediate state and high-cordierite (*cf.* spectrum VI). However, the half-intensity widths of the single bands as resolved through analysis increase considerably from "low" through intermediate state to high-cordierite thus resulting in a progressive overlap of the separate peaks observable in "low"-cordierite. It is this very effect of growing half-intensity width that is typical for increasing disorder in crystalline substances (Laves and Hafner 1956 and other references given previously). Therefore, the results of this infrared investigation confirm, independently of the results of X-ray studies, that the structural transition from high- to "low"-cordierite is caused principally by ordering processes.

For a more quantitative evaluation of the directly observable process of band splitting, six different splitting indices were defined using the band systems *A*, *C*, *E*, and *F* as shown in Figure 9. A similar procedure had been adopted by Hafner and Laves (1957) in their infrared studies of feldspars. The values of these six indices are plotted in the right hand portions of Figure 9 *versus* heating time of the samples. It can be readily seen that the main increases of the splitting indices take place within relatively short periods of heating at 1400°C, *i.e.* generally in less than 10 hours. By analogy with the results of other authors, these splitting indices are likely to represent a direct measure of the degree of order in the sample. Thus it is suggested that the process of ordering causing the infrared variations in pure Mg-cordierite is practically completed after some 10 hours of heating at 1400°C.

#### TENTATIVE INTERPRETATION OF SPECTRA

Infrared spectra of silicates, whether crystalline or not, display strong absorption in two different regions: near 1000  $\text{cm}^{-1}$  and 500  $\text{cm}^{-1}$ . These absorptions have first been interpreted as the two infrared-active vibration modes of a tetrahedral  $\text{TO}_4$  configuration by Schaefer, Matossi and Wirtz (1934). They attributed the 1000  $\text{cm}^{-1}$  absorption to the *T*-O stretching mode, the 500  $\text{cm}^{-1}$  absorption to the *T*-O bending mode. These two regions of absorption are subdivided in many crystalline silicates into complicated systems of separate bands. Although in most cases the reasons for these splittings are not known accurately, different central atoms of the tetrahedra, deviations of these tetrahedra from cubic symmetry as well as different kinds of linkage with neighbouring polyhedra may play a dominant role.

The two main silicate absorptions just discussed are found in the various spectra of the composition  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  as band systems *E*+*F* and *A*, respectively (Figs. 5 and 6), both of which are already

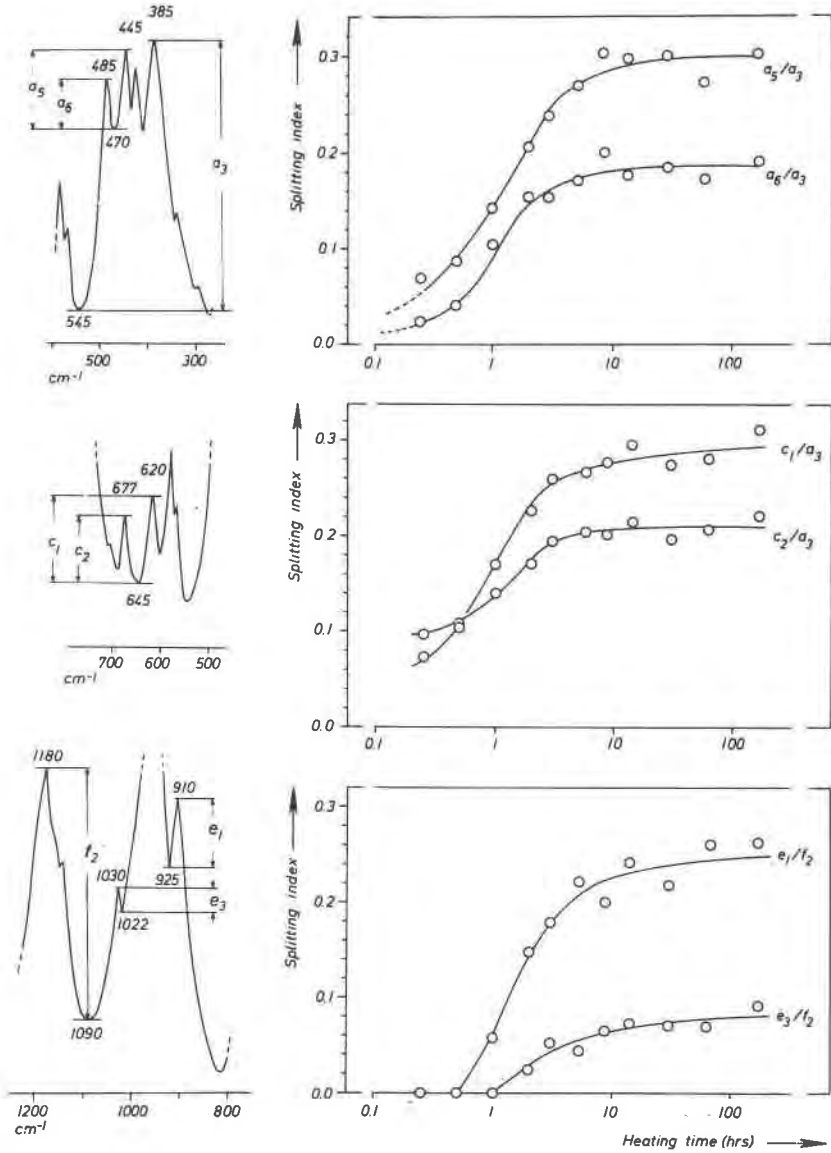


FIG. 9. Definition of six infrared splitting indices in band systems A, C, and E and their variations with heating time at 1400°C in a starting material of high-cordierite prepared from glass at 980°C, 305 hours. The reference values  $\alpha_3$  and  $f_2$  are taken from band systems A and F.

discernible in the glass (Fig. 5, I). The subdivision of the  $1000\text{ cm}^{-1}$  absorption into two separate systems *E* and *F*, also present in the glass, may possibly be due to the energy difference in the vibration of  $\text{SiO}_4$  versus  $\text{AlO}_4$  tetrahedra. If the empirical relationship found by Dachille and Roy (1959) between wavelength and nature as well as coordination of the central atom can be applied in the present case, the wave number for the  $\text{SiO}_4$  stretching mode may be calculated as  $1085\text{ cm}^{-1}$  and that for the  $\text{AlO}_4$  stretching mode as  $960\text{ cm}^{-1}$ . This is in fair agreement with the observed values in the band systems *E* and *F* for all the spectra measured (*cf.* Table 1).

Band system *D* has been interpreted by Bokii and Pliusnina (1958) and Pliusnina and Bokii (1958) as a characteristic feature of silicates such as cordierite containing six-membered rings. It is somewhat surprising, however, that this band has, in the present work, not only been found in the cordierite spectra (Figs. 5 and 6, III-X), but also, with lower intensity, in the spectrum of high-quartz<sub>ss</sub> (Fig. 5, II). For this latter material not containing six-membered rings, band *D* may, therefore, possibly be assigned to the symmetrical tetrahedral stretching mode activated by deviation of the tetrahedra from cubic symmetry as observed even in pure high-quartz (see Wyckoff 1963, p. 313-314).

For a possible assignment of band *B*, which is restricted to the spectra of the cordierites, it is important to note that the high-quartz structure apparently does not provide octahedral sites. By analogy with the structure of high-eucryptite (Winkler 1948, 1953), it was initially assumed that the high quartz<sub>ss</sub> of cordierite composition would contain Mg in tetrahedral coordination within the hollow spirals parallel to *c*. However, the most recent single-crystal work on a Mg-bearing high-quartz solid solution of a composition close to that of cordierite (H. Schulz and W. Hoffmann, pers. commun., 1969) indicates that Mg is located within the hollow spirals in a site providing approximately six-fold coordination. However, this site having *z* parameters 1/6, 3/6, or 5/6 is not octahedral (*cf.* Wyckoff 1963, fig. IV 39a). On the other hand, the cordierite structure does provide octahedral sites (Gibbs 1966), and band *B*, therefore, appears to represent an octahedral vibration. This conclusion is supported by the comparison of the calculated wave number of a  $\text{MgO}_6$  vibration ( $650\text{ cm}^{-1}$ ), again using the Dachille and Roy (1959) relationship, with the observed value ( $580\text{ cm}^{-1}$ ). On this basis the tentative assignment of band system *C* to octahedral vibrations seems justified as well. It must be emphasized that band systems *B* and *C* display the same kind of splitting in the course of the gradual ordering processes in the cordierite structure as all the other bands assigned to tetrahedral vibrations. Provided these band assignments are correct, this

still does not necessarily indicate that the octahedral sites are involved in the ordering mechanism. Splitting of octahedral vibration bands may be due solely to changes of point symmetry of the octahedral centroid by Al/Si ordering in the tetrahedral framework, since the octahedra have common edges with three neighboring tetrahedra and common corners with additional six tetrahedra.

#### COMPARISON OF POWDER X-RAY DIFFRACTION AND INFRARED RESULTS

In an effort to determine whether changes in the infrared properties during the thermal history of the cordierite are always accompanied by simultaneous variations of the powder X-ray diffraction patterns the following comparisons were made. The band located at  $1090\text{ cm}^{-1}$  between systems *E* and *F* in the high-cordierite sequence (Figs. 5 and 6, spectra III–VI) provides an example that a correlation is not always possible. In the X-ray patterns of the samples yielding these spectra no variations could be observed concomitant with the rise and fall of the absorption band discussed.

On the other hand, the strong increase of the infrared splitting indices (Fig. 9) within the first 10 hours of heating at  $1400^\circ\text{C}$  appears to be connected with a concomitant orthorhombic distortion of the structure as evidenced by the increase of the width index  $W_{1/3}$ , as well as, though less clearly discernible, of the distortion index  $\Delta$  (Fig. 4). For a more quantitative evaluation of these relationships the six previously defined splitting indices are plotted in Figure 10 against the width index. Except for one case, these plots do not show a simple linear relationship, but they are characterized by breaks at width indices between about  $0.30^\circ$  and  $0.45^\circ$ . According to Figure 4 these width indices would correspond to  $\Delta$  values of about  $0.10^\circ$  and  $0.17^\circ$ , respectively. Above these breaks a further increase of the width index is no longer accompanied by obvious changes of the splitting indices. If these splitting indices, however, are indeed a direct and independent measure of the degree of order in the sample as suggested in a previous section, one must conclude that a considerable portion of the orthorhombic distortion cannot be due to ordering, at least not to the type of ordering causing the infrared variations.

A similar discrepancy between infrared and X-ray properties has been found by Laves and Hafner (1962) in an adularia showing an infrared spectrum very similar to that of maximum microcline but with X-ray data of a monoclinic K-feldspar. As an explanation these authors proposed a domain structure for this mineral with the domains themselves exhibiting a rather high degree of order. This model, which was later confirmed by electron optical and diffraction methods (McConnell

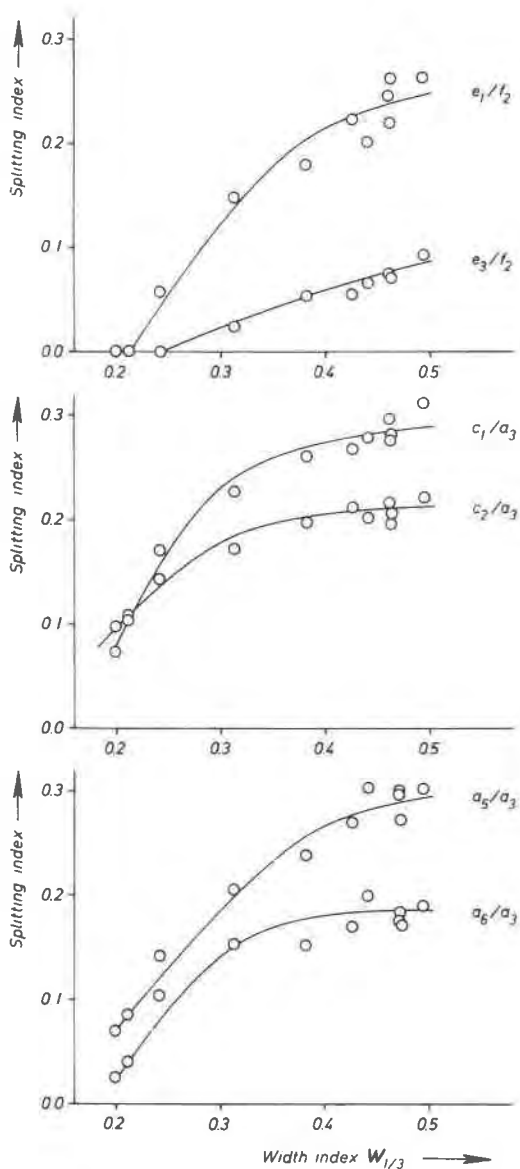


FIG. 10. Plot of infrared splitting indices measured after heating high cordierite at  $1400^\circ$  for various lengths of time (cf. Fig. 9) versus the width indices determined by powder X-ray diffraction methods in the same samples (cf. Fig. 4, which also shows the related distortion indices  $\Delta$ ). Note the discrepancy between orthorhombic distortion of cordierite structure and variations of infrared properties.

1965), implies that the infrared spectrum is sensitive to short-range order, whereas crystal symmetry as defined from X-ray diffraction patterns may also be influenced by long-range ordering processes.

The discrepancy between infrared and powder X-ray diffraction data as found in the present investigation indicates in a similar way that the high-“low” structural transition of Mg-cordierite taking place during heating of the metastable high form may involve two different processes of ordering following one another:

First, a short-range order process involving Al, Si, and, possibly, Mg, resulting in a domain structure. During this process the total variation of the infrared spectrum as well as a strong increase of width and distortion indices takes place.

Second, a long-range order process abolishing the domain structure and causing the final increase of width and distortion indices.

This interpretation seems to comply with the results of the single crystal work on Haddam cordierite by Meagher and Gibbs (1965) and Meagher (1967) which showed that complete Al/Si order is possible even in an intermediate state cordierite with  $\Delta=0.12^\circ$ . Because the orthorhombic distortion of cordierite thus appears to depend on both short-range and long-range order, it is clear that the distortion index  $\Delta$  cannot be used as a reliable measure of the degree of Al/Si order. This result is in contrast to the assumption made by Meagher (1967), that in isochemical situations the distortion index appears to have the capacity of indicating relative Si/Al disorder in cordierite, and that it becomes only ambiguous when the chemical variations of natural cordierites are taken into account. This assumption however, was incorrect in the first place because heating of the fully Al/Si-ordered Haddam cordierite sample with  $\Delta=0.12^\circ$  by Miyashiro (1957) to temperatures between 800 and 1300°C had already resulted in a strong increase of  $\Delta$ .

On the basis of the present study, it is suggested that splitting indices in infrared spectra of cordierite may be used as sensitive measures of the degree of cation short-range order. Further investigations will be necessary, however, in order to ascertain the influences of variable chemical composition on these infrared properties.

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