

CELL DIMENSIONS, MÖSSBAUER AND INFRARED-ABSORPTION SPECTRA OF SYNTHETIC CORDIERITE*

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ABSTRACT

Low cordierite compositions between the magnesium and iron end-members ($X_{\text{Fe}} = 0, 0.25, 0.50, 0.65, 1$) were synthesized in cold-seal vessels at 600 to 800°C and 0.1 to 0.2 MPa. Fugacities of H_2 and H_2O were controlled by the solid-phase buffer technique. Dehydrated phases were prepared from hydrothermal products by heating in a vacuum to 750 and 1150°C. X-ray powder-diffraction data indicate that low cordierite is orthorhombic; a , b and V increase and c decreases with increasing Fe content. Infrared-absorption spectra indicate that water is present as molecular H_2O in both Fe- and Mg-cordierite. Mössbauer spectra of synthetic cordierite and a natural Fe-rich cordierite indicate that Fe^{2+} in these specimens occupies sites in the framework rather than in the cavities.

Keywords: synthetic cordierite, iron cordierite, cell dimensions, infrared-absorption spectra, Mössbauer spectra.

SOMMAIRE

On a synthétisé, entre 600 et 800°C et entre 0.1 et 0.2 MPa, une série de compositions de cordiérite de basse température allant du pôle magnésien au pôle ferreux (X_{Fe} 0, 0.25, 0.50, 0.65 et 1) au moyen d'autoclaves à joint froid. Les fugacités de H_2 et H_2O étaient réglées par une technique où un assemblage de phases solides servait de tampon. Les phases déshydratées ont été préparées en chauffant les produits de synthèse hydrothermale *in vacuo* entre 750 et 1150°C. Les données de diffraction X (méthode des poudres) montrent une cordiérite de basse température (orthorhombique); a , b et V s'accroissent avec X_{Fe} tandis que c décroît. Les spectres d'absorption infrarouge montrent de l'eau à l'état moléculaire dans les deux pôles, ferreux et magnésien. Les spectres Mössbauer de la cordiérite synthétique et d'un échantillon naturel riche en fer montrent que le Fe^{2+} occupe des sites dans la charpente plutôt que dans les cavités.

(Traduit par la Rédaction)

Mots-clés: cordiérite synthétique, cordiérite ferreuse, paramètres réticulaires, spectre d'absorption infrarouge, spectre Mössbauer.

INTRODUCTION

The idealized composition of cordierite is $(\text{Me})_2\text{Al}_4\text{Si}_5\text{O}_{18}$, where *Me* represents almost exclusively magnesium and iron, with minor amounts of

manganese. Although it is rare to find natural cordierite with a ratio $\text{Fe}/(\text{Fe} + \text{Mg})$ greater than 0.5, synthetic cordierite can be produced over the entire Mg-Fe join. The mineral contains variable amounts of nonessential water [up to 4.8 wt. %: Leake (1960)], carbon dioxide and sodium.

Cordierite may occur in either a hexagonal or orthorhombic form. The hexagonal form, high cordierite or *indialite* (Meagher & Gibbs 1977), has been found only in fused sediments (Miyashiro & Iiyama 1954); it is the stable form above 830°C (Schreyer & Yoder 1964). The orthorhombic form, low cordierite, is the common polymorph found in nature.

The structure of low cordierite (Gibbs 1966) consists of a framework of four-membered rings of alternating AlO_4 and SiO_4 tetrahedra cross-linked with six-membered rings of $\text{Al}_2\text{Si}_4\text{O}_{18}$ composition. Apart from the adjacent Si atoms in the six-membered ring, there is perfect alternation of Al and Si atoms both laterally and vertically. All the octahedrally co-ordinated sites in low cordierite are equivalent by symmetry; therefore, Fe-Mg ordering caused by site preference is not considered likely. Structural studies by Meagher (1967), Cohen *et al.* (1977), Hochella *et al.* (1979), Wallace & Wenk (1980) and Armbruster & Bloss (1981) have confirmed the presence of nearly perfect Si-Al order in natural low cordierite.

One of the interesting aspects of the cordierite structure is the presence of cavities elongate parallel to the c axis and formed by adjacent six-membered rings. The cavities may be occupied by cations as well as CO_2 and H_2O . Sigiura (1959) and Iiyama (1960) suggested that two types of water are possible in cordierite: molecular water, present in the cavities, and bonded water, present as $(\text{OH})^-$ groups. Schreyer & Yoder (1964) concluded, from infrared-absorption studies of synthetic hydrous cordierite, that there is no evidence for bonded water. The structural studies of Gibbs (1966) and Cohen *et al.* (1977) confirmed the presence of molecular water in the cavities. The orientation of the water molecules within these cavities is still a matter of dispute, despite studies by Farrell & Newnham (1967) and Goldman *et al.* (1977) and neutron-diffraction studies by Cohen *et al.* (1977) and Hochella *et al.* (1979).

In addition, the cordierite problem is further complicated by the distribution and oxidation state of Fe in the structure. Fe^{2+} is a major constituent of

*Ottawa Carleton Centre for Geological Sciences Publication No. 15-84.

the octahedrally co-ordinated sites and may further occupy sites within the cavities, according to Duncan & Johnston (1974).

Synthetic magnesian cordierite has been extensively studied by Schreyer & Schairer (1961), Schreyer & Yoder (1964) and Medenbach *et al.* (1980). However, synthetic iron cordierite, although found as a phase in many experimental systems, has been less thoroughly studied. No information on the cell constants of cordierite of intermediate Fe/(Fe + Mg) has been previously reported. This study presents cell constants and X-ray-diffraction data for synthetic cordierite across the Fe-Mg join, and infrared-absorption spectra of the iron and magnesium end-members. Mössbauer spectra were obtained for a synthetic cordierite and a natural Fe-cordierite to determine the sites occupied by Fe²⁺.

SYNTHESIS OF CORDIERITE

The cordierite samples used in this study, having bulk compositions Fe/(Fe + Mg) of 0, 0.25, 0.50, 0.65 and 1, were synthesized hydrothermally using a modification of the gel technique of Boyd & Schairer (1964). The gels were produced from 'Analar' grade reagents that had been previously standardized. The sources of material are aluminum wire, iron sponge, magnesium oxalate and tetraethyl orthosilicate (T.E.O.S.). The iron end-member was also prepared from a mixture of kaolinite and synthetic fayalite. All compositions containing iron were reduced by heating at 600°C in a stream of hydrogen for several hours.

Cordierite was synthesized under controlled activities of water and hydrogen at temperatures between 500 and 800°C at pressures of 0.1 to 0.2 MPa in standard "Tuttle" type pressure vessels for periods of one to three days. Two methods of controlling the activities were used: the graphite-methane buffer G, CH(X,OH) and NNO, OH(GX,COH). The buffer notations are those of Eugster & Skippen (1967). The charges consisted of gel (or fayalite-kaolinite mix) plus approximately 20–25% water. Silver-palladium capsules were used for the G, CH(X,OH) buffer, and three concentric capsules (silver, silver-palladium and gold) for the NNO, OH(GX,COH) buffer, as described by Eugster & Skippen (1967). Anhydrous cordierite was prepared from the products of hydrothermal synthesis by heating in a vacuum to temperatures of 750°C or higher.

The run products were identified and checked for purity by X-ray diffraction and optical microscopy. A total of 107 samples of cordierite were prepared: 24 of Mg-cordierite, 60 of Fe-cordierite, 4 with a Fe/(Fe + Mg) of 0.25, 15 with a Fe/(Fe + Mg) of 0.50, and 4 with a Fe/(Fe + Mg) of 0.65. The material synthesized is fine grained and rarely well crystallized, with an average grain-size of 2 µm. Birefringence is weakly developed, and twinning is seen only occasionally in crystals of Mg-rich cordierite. Indices of refraction were measured on all synthetic materials. The purity of Mg-cordierite and cordierite with a Fe/(Fe + Mg) of 0.25 is better than 95%.

Lines of the quartz pattern were observed in the X-ray-diffraction patterns of cordierite with Fe/(Fe + Mg) ratios of 0.50, 0.65 and 1. Quartz occurs as

TABLE 1. CELL CONSTANTS FOR SYNTHETIC CORDIERITE

SAMPLE	Fe/(Fe+Mg)	Water Content	a (Å)	b (Å)	c (Å)	V (Å ³)	a - √3 b
1Co-S-2	0.0	0.32	17.010(7)	9.737(2)	9.343(3)	1547.3(4)	0.145
1Co-S-1	0.0	0.32	17.003(5)	9.735(1)	9.348(3)	1547.3(4)	0.145
1Co-S-12Q1TGA 1150°C	0.0	0.00	17.032(7)	9.789(7)	9.332(4)	1551.0(7)	0.129
1Co-S-12Q1TGA 750°C	0.0	0.00	17.025(8)	9.770(5)	9.335(3)	1554.0(9)	0.05
Schreyer & Yoder (1964)	0.0	unknown	17.06 (2)	9.72 (9)	9.33 (9)	1547.0(4)	-
2Co-S-1	0.25	0.40	17.025(7)	9.742(3)	9.339(3)	1548.9(5)	0.152
2Co-S-2TGA	0.25	0.00	17.025(8)	9.770(5)	9.329(4)	1551.8(5)	0.101
3Co-S-5	0.50	0.44	17.059(8)	9.814(4)	9.313(2)	1556.1(5)	0.06
3Co-S-12-1	0.50	0.61	17.060(5)	9.795(4)	9.307(2)	1552.2(5)	0.094
3Co-S-12-2	0.50	0.61	17.049(5)	9.814(3)	9.317(2)	1559.9(3)	0.05
3Co-S-2TGA 850°C	0.50	0.00	17.100(13)	9.789(7)	9.314(3)	1559.0(6)	0.145
4Co-S-1	0.65	0.40	17.104(7)	9.785(4)	9.313(2)	1558.8(5)	0.155
4Co-S-2TGA 900°C	0.65	0.00	17.114(9)	9.797(5)	9.307(3)	1560.5(5)	0.144
Co-S-10	1.00	0.33	17.207(7)	9.854(4)	9.289(2)	1574.9(4)	0.14
Co-S-20	1.00	0.38	17.195(8)	9.842(5)	9.292(2)	1572.6(4)	0.147
Co-S-28	1.00	0.61	17.195(4)	9.840(2)	9.296(2)	1573.0(3)	0.151
Co-S-34	1.00	0.52	17.188(4)	9.850(3)	9.295(2)	1573.6(5)	0.126
Co-S-36	1.00	0.45	17.215(10)	9.839(4)	9.293(3)	1574.0(7)	0.173
Hsu (1968)	1.00	unknown	17.17 (7)	9.86 (5)	9.28 (3)	1574 (5)	-
Co-S-36TGA 900°C	1.00	0.00	17.198(9)	9.862(7)	9.292(3)	1576.0(7)	0.116

Figures in parentheses are standard deviations.

Water content of synthetic cordierite was determined by thermogravimetric analysis

minute inclusions within the cordierite grains and is commonly associated with greenish inclusions of an isotropic substance of high index of refraction. In the experiments designed to synthesize Fe-cordierite, this impurity was identified as hercynite FeAl_2O_4 on the basis of index of refraction (approximately 1.8) and isotropism. The amount of this impurity in Fe-cordierite may be as high as 15–20%. However, as there is no Mg present, all cordierite in these experimental products probably has the composition of the pure Fe end-member.

X-RAY DIFFRACTION

X-ray powder-diffraction photographs were prepared from four samples of Mg-cordierite, eight of intermediate composition and six samples of Fe-cordierite from both hydrous and anhydrous materials. The powder-diffraction data for hydrous Fe-cordierite and intermediate cordierite with $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.25$ have been deposited with the National Research Council of Canada. These tables are available, at nominal cost, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. The X-ray lines may be indexed on the basis of an orthorhombic cell, and the least-squares refinement of the cell constants converged rapidly. In contrast, refinement based on a hexagonal cell resulted in poor convergence. Thus, orthorhombic symmetry is assumed to be correct for synthetic cordierite. This is supported by infrared-absorption studies and by measure-

ments of the width index (Langer & Schreyer 1969), which may be correlated with the distortion index of Miyashiro (1957).

The refined cell-constants of eighteen samples of synthetic cordierite are compared in Table 1 with those for a Mg-cordierite given by Schreyer & Yoder (1964) and those for a Fe-cordierite given by Hsu (1968). The parameter $a - \sqrt{3}b$ is also given in Table 1 to indicate the deviation of the cell from hexagonal geometry.

INFRARED-ABSORPTION SPECTROSCOPY

Infrared-absorption spectra were obtained on iron and magnesium end-members to determine the nature of water in the structure and to confirm the symmetry of the synthetic samples. The spectra were run on a Perkin-Elmer infrared spectrophotometer (model 225). Polystyrene was used for calibration.

Infrared-absorption spectra (Fig. 1) of both iron and magnesium hydrous cordierite in the region 1200–4000 cm^{-1} indicate a broad band between 3200 and 3600 cm^{-1} , and additional bands at 1650, 2930 and 3690 cm^{-1} . These bands are similar to those found in this region by Schreyer & Yoder (1964) on a synthetic hydrous Mg-cordierite and a natural cordierite containing 1.62 wt. % water. All these bands, except that at 3690 cm^{-1} , were attributed to the presence of molecular water (Farrell & Newnham 1967).

The band at 3690 cm^{-1} could either indicate absorbed water or the presence of tetrahedrally bonded

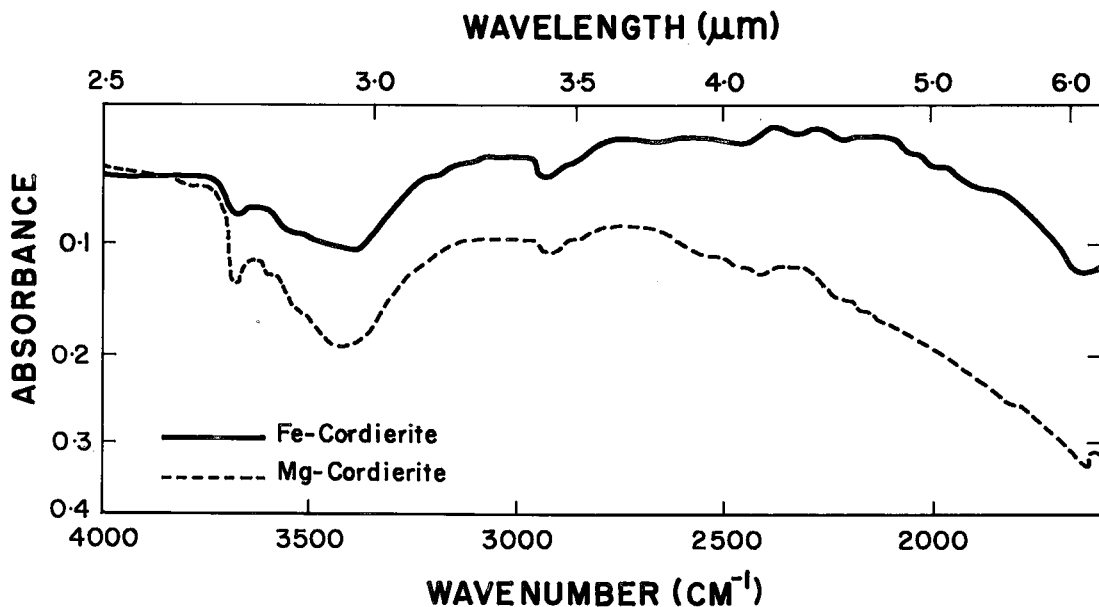


FIG. 1. Infrared-absorption spectrum of Mg- and Fe-cordierite in the range 1600–4000 cm^{-1} .

(OH)⁻ in the cordierite structure. To clarify the origin of this band, additional spectra were obtained in the vicinity of 3690 cm⁻¹ (Gunter 1977) for dehydrated cordierite that had been heated to either 750 or 1150°C during thermogravimetric analysis. The band at 3690 cm⁻¹ is missing in all spectra of dehydrated samples, indicating that in the hydrous samples it represents absorbed H₂O and not structural (OH)⁻. This conclusion is similar to that reported by Schreyer & Yoder (1964), Gibbs (1966), Farrell & Newnham (1967) and Cohen *et al.* (1977).

Langer & Schreyer (1969) showed that the hexagonal - orthorhombic transition from high cordierite to low cordierite causes splitting of infrared-absorption bands in the 300-1200 cm⁻¹ region (Table 2). The infrared-absorption spectra of cordierite synthesized in this study are closely comparable with the spectra of Langer & Schreyer for an intermediate-state cordierite with a distortion index Δ of 0.09°, thus confirming the results of the X-ray study that the cordierite synthesized in this work is orthorhombic.

MÖSSBAUER SPECTRA

Mössbauer spectra of a synthetic hydrous cordierite of composition Fe/(Fe + Mg) = 0.25 and a natural iron-rich cordierite [Fe/(Fe + Mg) = 0.9] from Dolni Bory, Czechoslovakia, were obtained from weighed samples pressed between two cellulose tapes and mounted on a perforated cardboard disc. The amount of sample used varied between 10 and 25 mg. Spectra were analyzed by fitting Lorentzian

TABLE 2. INFRARED-ABSORPTION BANDS OF SYNTHETIC CORDIERITE IN THE 300-1200 cm⁻¹ REGION

Band System	Langer & Schreyer (1969)		This study
	Hexagonal high cordierite cm ⁻¹	Intermediate-state cordierite $\Delta = 0.09$ cm ⁻¹	Fe-cordierite $\Delta = 0.10$ cm ⁻¹
A	387	297	300
	429	344	355
		386	390
	463	426	430
B		449	455
	578	486	475
		569s	565
C		582	580
	628	621	670
		679	
D	677	705svw	690
	768	752	750
		771	785
E	957	911	895
		958	960
		1029	1020
F	1090		
		1145s	1140
		1165s	1170
	1175	1182	

Band-system notations are from Langer & Schreyer (1969).
s = shoulder, vw = very weak.

curves to the experimental points by use of a non-linear least-squares-regression program.

Mössbauer spectra of natural cordierite have been previously studied by Duncan & Johnston (1974) and Goldman *et al.* (1977), but no spectra seem to have been published of synthetic cordierite. Mössbauer studies by Duncan & Johnston (1974) on oriented sections of a natural cordierite containing 1.85 wt.% iron suggest that 80% of Fe is present as Fe²⁺ in the octahedral site, 18% as Fe²⁺ in a nonoctahedral site (presumably the cavities) and 2% as Fe³⁺ in a tetrahedral site. On dehydration, the Fe²⁺ attributed to the second site is believed to be removed and replaced by an equivalent amount of Fe³⁺ without apparent change in the structure of the mineral. To account for the relative ease with which this Fe can be oxidized and to further account for the preservation of the structure in spite of oxidation of 18% of the total Fe, Duncan & Johnston (1974) concluded that this iron occupies a site in the cavities. Goldman *et al.* (1977) studied Mössbauer spectra of a number of pulverized samples of natural cordierite, including a sample used by Duncan & Johnston. Contrary to the finding of Duncan & Johnston, Goldman *et al.* found that less than 5% of the iron occurs in the cavities; on the basis of optical-absorption spectroscopy and the powder Mössbauer spectra, they concluded that this iron is nonstructural.

Both Mössbauer spectra obtained in the present study show simple quadrupole-split spectra with an isomer shift characteristic of high-spin Fe²⁺ in octahedral sites. The isomer shift relative to metallic iron and the quadrupole splitting are 1.213 and 2.193 mm/s for the natural cordierite and 1.182 and 2.257 mm/s for the synthetic cordierite with a ratio Fe/(Fe + Mg) of 0.25. There is no evidence of significant amounts of Fe in the cavities. It is possible that spectra obtained from oriented samples of single crystals would show the presence of a weak doublet attributable to minor amounts of Fe in cavity sites. For the natural Fe-rich specimen and for the synthetic cordierite examined in this study, Fe is present almost exclusively as Fe²⁺ in the octahedral sites.

DISCUSSION

Natural cordierite can accommodate many chemical species in its channel cavities, for example, H₂O, CO₂, He, Ar and small amounts of hydrocarbons as well as Na⁺ (Armbruster & Bloss 1982). This makes it difficult to distinguish the often conflicting effects of the different species on cell constants and the distortion index. The synthetic samples of cordierite examined in this study were prepared without species other than Al, Si, Fe, Mg and H₂O. The only possible gaseous constituent in the cavity is H₂O.

The cell constants determined can be compared with those obtained in a study of 11 natural specimens ranging in Fe/(Fe + Mg) from 0.05 to 0.90 (Selkregg & Bloss 1980). For both natural and synthetic samples, the parameters a , b and V increase as c decreases with increase in Fe/(Fe + Mg). In both studies, the cell volume increased when cordierite was dehydrated. Selkregg & Bloss (1980) also calculated a distortion index to measure the deviation of the cell from hexagonal geometry, and found that for three of the four samples from which cell constants of dehydrated material were obtained, the distortion index increased. This indicates an increasing departure from hexagonal geometry. In contrast, 5 of the 6 dehydrated samples of synthetic cordierite prepared in this study moved closer to hexagonal geometry, as measured by the term $a-\sqrt{3}b$. This may be due to the retention of Na⁺ in the structure of natural cordierite after dehydration, whereas the synthetic cordierite contains no Na⁺.

Stout (1975) suggested that the presence of water in the ring cavities causes the channels to collapse around the c axis. He further suggested that removal of water would force the ring tetrahedra apart, lengthening a with respect to b , and thus would increase both the distortion index and the quantity $a-\sqrt{3}b$. Except for the composition Fe/(Fe + Mg) = 0.50, the quantity $a-\sqrt{3}b$ decreases on dehydration. Therefore, the synthetic compositions do not appear to follow the model suggested by Stout (1975). The cell constants of the hydrous iron cordierite (this study) have been obtained from specimens with a variety of water contents, but no systematic variation of cell constants with water content was detected.

The infrared-absorption spectrometric results (this study) confirm that H₂O in synthetic cordierite is molecular, and can be driven off by heating to 750°C. This conclusion applies to the Fe end-member as well as to more magnesian compositions.

Mössbauer studies of synthetic cordierite and a natural sample of Fe-rich cordierite from Dolni Bory are consistent with previous results obtained by Goldman *et al.* (1977) from spectra of natural cordierite. The results of the present study show that very little Fe²⁺ occurs within cavities in the structure of the two specimens examined.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. B. Chang, of the Department of Chemistry, Carleton University, for assistance in preparing the infrared-absorption spectra and to Dr. C. Bordeleau, of the same department, for assistance in preparing the Mössbauer spectra. Dr. R.S. Dean, Mines Branch, Department of Energy, Mines and Resources, kindly provided the kaolinite used in the synthesis of Fe-cordierite. A

sample of natural cordierite from Dolni Bory, Czechoslovakia, was obtained from the Carleton University Mineral Collection. This research was supported by NSERC grants A4253 to G.B. Skippen and A5113 to G.Y. Chao. The manuscript benefitted from criticism by two anonymous referees and the editorial staff of the journal.

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Received August 4, 1983, revised manuscript accepted December 21, 1983.