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The mechanism and kinetics of Al,Si ordering in Mg-cordierite

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Abstract

Under non-equilibrium conditions the hexagonal to orthorhombic ordering transformation in Mg-cordierite takes place via a continuous mechanism involving the development of a metastable short-range-ordered modulated structure. A Time–Temperature–Transformation diagram illustrates the kinetics of this transformation sequence. The activation energy for the formation of the modulated microstructure is found to be 120±10 kcal/mole (500±40 kJ/mole) consistent with Al,Si ordering as the rate-limiting process. X-ray diffractrometry, transmission electron microscopy and IR spectrometry have been used to trace the development of short-range and long-range order in cordierite. They show that ordering proceeds smoothly with time. Short-range ordering is well-developed by the time the modulated microstructure forms, and continued annealing increases the long-range ordering to a point where it is sufficiently well-developed to be seen in X-ray diffraction studies.

Introduction

Mg-cordierite, $Mg_2Al_4Si_5O_{18}$ occurs in two polymorphic forms. In the high temperature hexagonal structure, space group *P6/mcc*, stable above about 1450°C (Schreyer and Schairer, 1961; Putnis, 1980a) the Al and Si atoms are distributed over two sets of tetrahedral sites—three T_1 and six T_2 sites per formula unit. Meagher and Gibbs (1977) in a structure refinement of indialite, the natural hexagonal polymorph, found that the Al,Si distribution involved two Al and one Si atoms disordered over the T_1 sites and two Al and four Si atoms disordered over the T_2 sites. Within the hexagonal space group a fully ordered configuration of Al and Si is not possible.

In the slightly distorted, low-temperature orthorhombic form, space group *Cccm*, the T_1 sites are split into two non-equivalent sites T_11 and T_16, while the T_2 sites are split into three non-equivalent sites T_21, T_26 and T_23 (Meagher and Gibbs, 1977). Within this new structure the Al,Si atoms are able to form a completely ordered distribution. X-ray and neutron diffraction studies of orthorhombic cordierites (Gibbs, 1966; Cohen *et al.*, 1977) confirm a completely ordered configuration with Al in the T_11 and T_26 tetrahedra and Si in the T_16, T_21 and T_23 tetrahedra.

Thus the hexagonal–orthorhombic transition in Mg-cordierite is associated with Al,Si ordering. Under non-equilibrium conditions this ordering transition takes place by an apparently continuous mechanism via a sequence of intermediate structural states characterized by the distortion index Δ, based on the splitting of X-ray powder diffraction peaks (Miyashiro, 1957). The value of Δ ranges from 0.0 in hexagonal cordierite to about 0.25 in fully ordered, orthorhombic Mg-cordierite. However, the structural change $P6/mcc \rightarrow Cccm$ has been shown to be first order with a first order discontinuity of $\Delta \approx 0.25$ associated with the distortion (Putnis, 1980a). This indicates that the intermediate states are metastable and that the apparently continuous sequence from high to low cordierite necessarily implies the existence of a short-range-ordered domain structure. This domain structure has been described by Putnis (1980a,b).

The aim of this paper is to present data on the kinetics and mechanism of the transition and to describe a combined transmission electron micros-

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copy, infrared spectroscopy and X-ray diffraction study of the onset of short-range order in hexagonal cordierite and the subsequent development of long-range order in orthorhombic cordierite. This is an extension of earlier X-ray and infrared studies on synthetic cordierites by Langer and Schreyer (1969), who found that the high to low transition in cordierite involved first a short-range ordering process and then the development of long-range order with time.

Experimental

The starting material for the experimental runs was stoichiometric Mg-cordierite glass. The method of preparation of the glass and its chemical analysis have been described elsewhere (Putnis, 1980a).

The glass was devitrified by annealing in air at temperatures between 1050°C and 1445°C for periods from 30 seconds to 1000 hours. In all cases the first crystallization product was hexagonal cordierite which on annealing ultimately transformed to orthorhombic cordierite. The run products were examined by X-ray powder diffractometry, transmission electron microscopy (TEM) and IR spectroscopy. TEM was carried out on crushed grain mounts in a JEM 100CX electron microscope operating at 100kV. The IR spectra were obtained using the KBr pellet technique and a Nicolet FTIR spectrometer. The cordierite was ground in a tungsten carbide mortar and pestle, and care was taken to assure that the powders were of approximately the same particle size.

Results

The kinetics of the hexagonal-orthorhombic transition

Figure 1 shows a plot of the experimental runs on a Time–Temperature–Transformation diagram. In each case the microstructure was characterized by TEM, and the progress of the transformation averaged over the sample as a whole was monitored by measuring the splitting of the $(211)_{\text{hex}}$ peak in the X-ray powder diffractometer trace. This splitting into the (131), (511) and (421) orthorhombic peaks defines the distortion index (Miyashiro, 1957):

$$\Delta = 2\theta_{131} - \frac{2\theta_{511} + 2\theta_{421}}{2}.$$

The limitations and physical significance of the Δ index in this context have been discussed by Putnis (1980a).

The area of the TTT diagram labelled *hexagonal* describes the temperature–time region in which the hexagonal cordierite shows no microstructural evidence of transformation, *i.e.*, the sample is homoge-

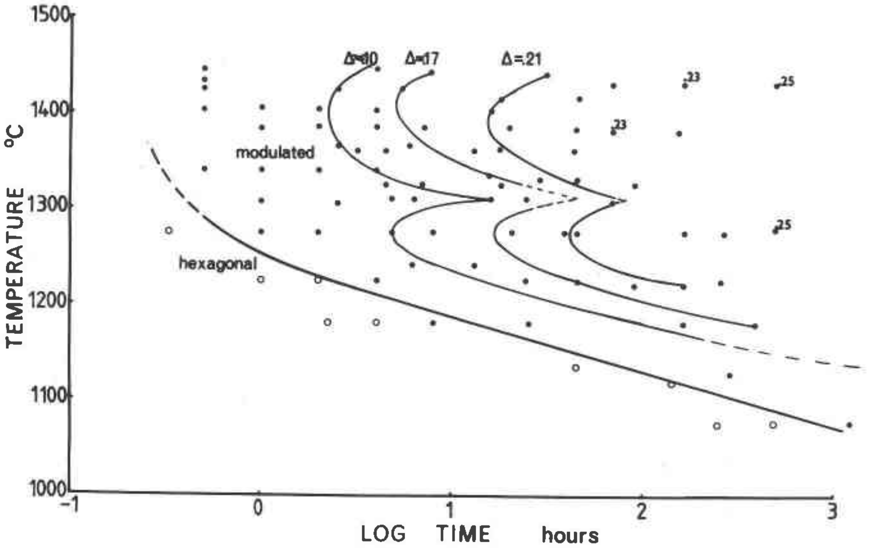

Fig. 1. A Time-Temperature–Transformation (TTT) diagram for the hexagonal–orthorhombic transformation in Mg-cordierite. The points represent runs examined by both X-ray powder diffraction and TEM. In the region labelled *hexagonal* (open circles) the cordierite has no microstructure. In the *modulated* region the hexagonal cordierite has a "tweed" microstructure visible in the TEM. The first measurable splitting of the powder diffraction peaks is marked by the double C curve labelled Δ ≈ .10. Lines of equal Δ value are drawn for Δ = .17 and Δ = .21. Points to the right of Δ = .21 have larger Δ values, some of which are marked.

neous on an electron microscope scale. Thus the effective cut-off for the transformation on a laboratory time scale is about 1000°C.

In the region labelled *modulated* the hexagonal material develops a characteristic tweed-like microstructure, evident in transmission electron micrographs (see Fig. 3 in Putnis, 1980a). The modulation consists of two orthogonal distortion waves lying on a pair of planes of the type {100} and $\{1\bar{2}0\}$. Dark field imaging shows that the distortion waves are transverse in character with the amplitude vectors lying in the (001) plane. At this stage there is no evidence for any departure from hexagonal symmetry. X-ray diffractometry shows no peak splitting. Selected area electron diffraction patterns sampling areas 1000Å in diameter show no splitting of spots, indicating that on this scale the material is hexagonal.

Annealing for longer periods results in a coarsening of the modulated structure and eventually the first signs of splitting of the $(211)_{hex}$ peak on the diffractometer trace. The smallest measurable value of Δ in the present study is about 0.10. Continued annealing increases the Δ value to a maximum of about 0.25. The increase in Δ may be associated with a coarsening process which has been described by Putnis (1980a).

On Figure 1 contours of equal Δ value (chosen arbitrarily to be $\Delta = 0.10, 0.17, 0.21$) indicate the presence of two lobes on the diagram with a fairly sharply defined boundary between them at around 1310°C. This suggests that the transformation of the modulated hexagonal structure to the orthorhombic structure takes place by two different, temperature-dependent mechanisms.

Electron microscopy of samples annealed at temperatures above and below 1310°C confirm the existence of two mechanisms for the transformation. These two mechanisms were described by Putnis (1980a, Fig. 3), although the temperature dependence was not defined. At high temperatures the mechanism is markedly heterogeneous, involving the apparent nucleation of orthorhombic cordierite from the modulated hexagonal matrix. At temperatures below 1310°C the transformation process appears to be more homogeneous in that it involves an overall coarsening of the modulation and a progressive loss of the component lying on $\{1\bar{2}0\}$. The two mechanisms may, in a general way, be identified with heterogeneous and homogeneous nucleation of orthorhombic cordierite from a modulated hexagonal matrix.

The activation energy for the formation of modulated cordierite

The slope of the boundary in Figure 1 between hexagonal and modulated cordierite may be used to calculate the overall activation energy for the process which is responsible for the formation of the modulation. The method used has been described by Putnis and McConnell (1980, p. 146) and gives a value of 120±10 kcal/mole (500±40 kJ/mole). The significance of this result is that it establishes that the rate controlling step in the formation of the modulation is one with a high activation energy consistent with Al,Si ordering and is not due primarily to a structural collapse. Based on this evidence, coupled with the nature of the microstructure, it is assumed that the modulation involves a sinusoidal variation in the degree of order, the maxima and minima of the modulation representing twin-related distributions of Al and Si.

Such behavior is consistent with the existence of a strongly first-order phase transformation from hexagonal to fully ordered orthorhombic cordierite at about 1450°C. The temperature independence of the equilibrium Δ value of 0.25 also indicates that below 1450°C the stable state has lattice parameters consistent with a completely ordered Al/Si distribution (Gibbs, 1966; Cohen *et al.*, 1977). When there is a large discontinuity in the degree of order at the equilibrium temperature (Putnis, 1980a), only a limited range of equilibrium states of intermediate order are possible. However, under metastable conditions a kinetically more favorable alternative to nucleation of the fully ordered structure involves the formation of order modulations in which considerable local or short-range order may be achieved by utilizing the statistically equivalent ordered distributions available. In this way a substantial reduction in free energy may result, although the long-range order is zero and the symmetry of the structure remains hexagonal.

The development of short-range order

To obtain information on the development of short-range order in the initial stages of the transformation, a sequence of annealing runs was carried out at 1200°C for annealing times from 0.5 minutes (after 1.5 minutes to achieve thermal equilibrium) to 100 hours when splitting of the X-ray powder peaks is first observable.

At 1200°C crystallization of the cordierite glass is virtually instantaneous and no glass could be detected in the run product by TEM in the 0.5 minute runs. The crystalline material is hexagonal cordierite with no microstructure. The onset of an observable modulated microstructure occurs after 3 hours of annealing. In these early stages the modulation is of low amplitude with a wavelength of about 100Å, although this wavelength is not very well defined. Continued annealing for an additional 2–3 hours increases the amplitude of the modulation to its maximum value. Coarsening of the modulation begins after about 20 hours and continues until the formation of orthorhombic cordierite is detectable by powder diffractometry. The coarsening is accompanied by the development of discrete twin planes on $\{110\}_{ortho}$ and $\{310\}_{ortho}$ with the eventual domination of the former composition plane.

Figure 2 contrasts the time scales over which X-rays and TEM are effective methods of characterization of the structural state. By the time that X-ray splitting is observable, the modulated microstructure has coarsened to a scale of >1000Å.

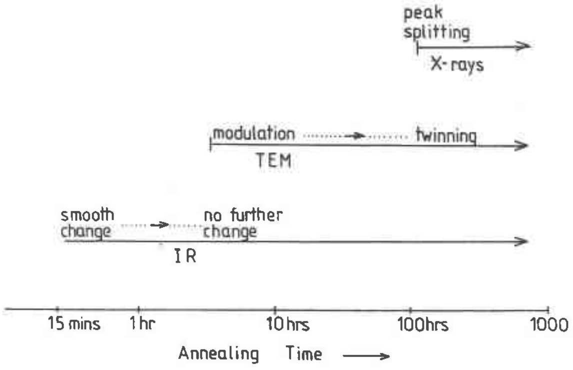

Fig. 2. The time scale over which X-ray, TEM and IR techniques are relevant in characterizing the hexagonal–orthorhombic transition in cordierites annealed at 1200°C. Major changes in the IR spectrum take place between 0 and 4 hours. A modulation appears in the TEM after 3 hours and coarsens to a twinned domain structure (>1000Å) by the time X-ray diffraction records any deviation from hexagonal symmetry (after 100 hours).

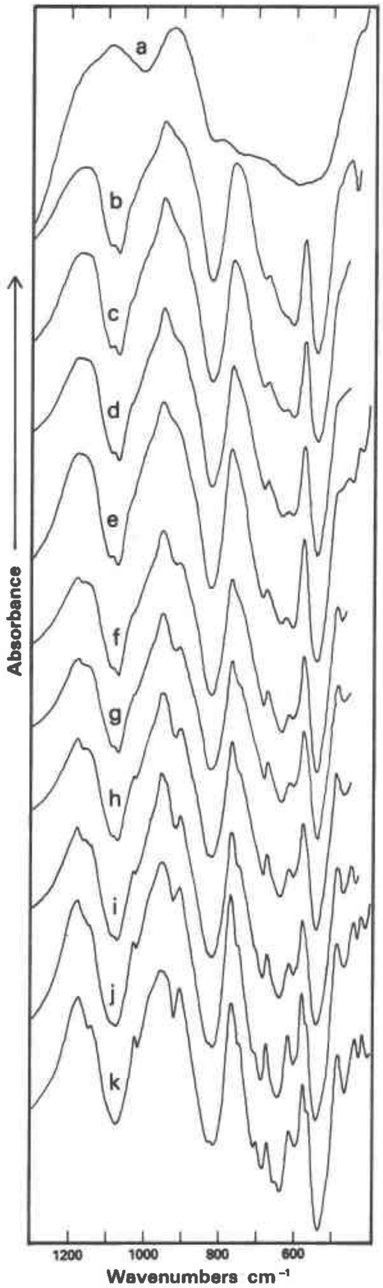

Fig. 3. Infrared absorption spectra of cordierite glass (a) and cordierite annealed at 1200°C for 0.5 min. (b), 5 min. (c), 30 min. (d), 1 hr. (e), 2 hr. (f), 4 hr. (g), 8 hr. (h), and 16 hr. (i). Spectrum (j) is cordierite annealed at 1380°C for 145.5 hr., and spectrum (k) is natural cordierite from Mt. Milton, Australia.

Because IR spectra reflect short-range interactions, a comparison of the degree of local Al,Si order in samples annealed for different times at 1200°C was made by comparing their IR spectra (Fig. 3) with the IR spectrum of fully ordered synthetic Mg-cordierite (annealed at 1380°C for 150 hours). IR spectra of several natural cordierites were also recorded. The spectrum of the material annealed for 0.5 minute is quite different from that of the glass, with the 1090 cm^{-1} band shifted to 1160 cm^{-1} and a strong absorption band appearing at about 760 cm^{-1}. With increased annealing time, the major changes appearing are a pronounced sharpening of absorption bands and the development of discrete absorptions in the regions 600–700 cm^{-1}, 730–760 cm^{-1}, 890–1030 cm^{-1}, and 1140–1180 cm^{-1}. The bands in these regions develop smoothly with time, and no major changes in the spectra occur after 5 hours annealing. This correlates with the observation by TEM that the modulated microstructure becomes visible after 3 hours and has attained its maximum amplitude after 5 hours. Comparison of the spectra of modulated hexagonal cordierite and fully ordered orthorhombic cordierite shows no significant differences, strongly suggesting that the modulated cordierite has a high degree of short-range order. Also, the spectrum of fully ordered synthetic cordierite is not significantly different from spectra of several natural cordierites, one of which is presented in Figure 3. These observations are in good agreement with Raman spectroscopic measurements showing the maximum development of short-range ordering when the modulations have reached their maximum amplitude (P. McMillan, pers. comm.).

Discussion

The combination of XRD, TEM and IR techniques allows the following general description to be made of the structural changes taking place in synthetic Mg-cordierite crystallized from glass and annealed at 1200°C.

The first material to crystallize from the glass is hexagonal cordierite with a local structure very different from the parent glass structure. While the present techniques do not enable any estimate to be made of the degree of Al,Si order in this first formed cordierite, we assume that a certain amount of short-range order inevitably exists. A smooth and progressive increase in the degree of short-range order with annealing time is evident from the changes in the IR spectra. The short-range order involves the development of incipient domains in which the Al,Si distribution is associated with twin-related local distortions which are statistically equivalent and consistent with the hexagonal symmetry of the crystal as a whole. These distortions take the form of two orthogonal transverse waves utilizing two of the possible three orientational variants associated with the hexagonal-orthorhombic transition.

At a point where the degree of short-range order is sufficiently well established, the distortion waves have large enough amplitude to produce strain diffraction contrast in the TEM image. No discontinuity in the degree of order is apparent at the onset of the modulation, as detected by TEM, and in this sense the line drawn on the TTT diagram in Figure 1 separating the *hexagonal* from the *modulated* region has no fundamental significance. However, it is reasonable to assume that it represents the development of an equal degree of short-range order in the samples, and is useful as a marker for the kinetic study.

The primary effect of continued annealing is to produce coarsening in the microstructure which in effect is a change from short-range to long-range order. The fact that the IR spectra show no further change during this process strongly suggests that the degree of short-range order is not significantly increased. The relaxation of strain and the reduction of the total area of domain boundaries during coarsening will, however, allow a further slight increase in the degree of order.

As coarsening necessarily implies the redistribution of domains of different orientations, an imbalance in the degree of coarsening of different domains will lead to a loss of hexagonal symmetry in the crystal as a whole. X-ray powder diffractometry is a relatively insensitive tool to measure small average distortions in the structure, and TEM shows that coarsening has proceeded to a large extent before splitting of the diffractometer peaks can be detected. Armbruster and Bloss (1981) have demonstrated that changes in the optic axial angle $2V$ are very much more sensitive to such small distortions and have reported large increases in $2V$ of flux-grown Mg-cordierite which were still X-ray hexagonal.

Continued coarsening of the microstructure can be correlated with a smooth change in the distortion index Δ until ultimately the maximum value of 0.25 is reached. This sequence has been discussed by Putnis (1980a).

Finally, it is relevant to note that in this paper the terms hexagonal cordierite, modulated hexagonal, and orthorhombic cordierite are used as convenient labels for describing the progress of the transformation by the methods employed here and do not imply a strictly rigorous definition of the point in the sequence when the symmetry change takes place. In a continuous transformation of this kind it is not a trivial matter to define the point at which the cordierite becomes orthorhombic, and it depends to a certain extent on the scale being considered and the methods used to detect symmetry changes. Clearly, the existence of a $2V$ angle in X-ray hexagonal cordierite indicates that it is already orthorhombic, while the presence of two orthogonal modulations necessarily demands a reduction in point group symmetry. The distortions involved in the coexistence of twin related domains in the modulation are also accompanied by an overall lattice distortion which is a necessary component in the formation of the modulation (McConnell, in prep.). In this respect it may well be that if hexagonal cordierite (*sensu stricto*) is unstable to orthogonal distortion waves, then rigorously speaking it could be considered to be orthorhombic throughout the whole of the ordering sequence described here.

Conclusions

A primary aim of this work is to demonstrate the importance of short-range order and the methods which may be used to characterize it qualitatively. Figure 2 shows the relative ranges in which the different techniques employed here have provided information on the structural state of the cordierites studied. Short-range order is particularly important in the study of the thermochemistry of silicates, as Al,Si order-disorder is normally accompanied by considerable enthalpy effects (Navrotsky and Kleppa, 1973; Putnis 1980b). This work emphasizes the need for careful characterization of materials used in calorimetric investigations.

The mechanism of Al,Si ordering in Mg-cordierite under non-equilibrium conditions is relevant to the general problem of metastable behavior in a situation where the equilibrium transformation involves a major first-order phase change. The situation in cordierite is analogous to that in K-feldspar, where sanidine and microcline are the two stable disordered and ordered polymorphs, respectively. The metastable transformation involving the formation of orthoclase and the intermediate microclines similarly involves the growth of short-range-ordered domains in a modulated microstructure (McConnell, 1971; Putnis and McConnell, 1980). The high equilibrium order–disorder temperature in cordierite, however, allows this metastable region to be explored experimentally, whereas in K-feldspar, no similar experiments are kinetically possible.

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References

Armbruster, T. and Bloss, F. D. (1981) Mg-cordierite: Si/Al ordering, optical properties, and distortion. Contributions to Mineralogy and Petrology, 77, 332–336.

Cohen, J. P., Ross, F. K., and Gibbs, G. V. (1977) An X-ray and neutron diffraction study of hydrous low cordierite. American Mineralogist, 62, 67–78.

Gibbs, G. V. (1966) The polymorphism of cordierite I: The crystal structure of low cordierite. American Mineralogist, 51, 1069–1081.

Langer, K. and Schreyer, W. (1969) Infrared and powder X-ray diffraction studies on the polymorphism of cordierite, $Mg_2(Al_4Si_5O_{18})$. American Mineralogist, 54, 1442–1459.

McConnell, J. D. C. (1971) Electron optical study of phase transformations. Mineralogical Magazine, 38, 1–21.

Meagher, E. P. and Gibbs, G. V. (1977) The polymorphism of cordierite II: The crystal structure of indialite. Canadian Mineralogist, 15, 43–49.

Miyashiro, A. (1957) Cordierite–indialite relations. American Journal of Science, 255, 43–62.

Navrotsky, A. and Kleppa O. J. (1973) Estimate of enthalpies of formation and fusion of cordierite. Journal of the American Ceramic Society, 56, 198–199.

Putnis, A. (1980a) The distortion index in anhydrous Mg-cordierite. Contributions to Mineralogy and Petrology, 74, 135–141.

Putnis, A. (1980b) Order-modulated structures and the thermodynamics of cordierite reactions. Nature, 287, 128–131.

Putnis, A. and McConnell, J. D. C. (1980) Principles of Mineral Behaviour. Elsevier, New York.

Schreyer, W. and Schairer, J. F. (1961) Compositions and structural states of anhydrous Mg-cordierites: a reinvestigation of the central part of the system $MgO–Al_2O_3–SiO_2$. Journal of Petrology, 2, 324–406.

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