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A high-pressure phase transition in cordierite

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Abstract

This note reports a high-pressure phase transition in cordierite detected with a volumetric technique in isothermal compression experiments carried out in a piston-cylinder high-pressure apparatus. Transition data at 25, 510, 600, 730 and 900°C were obtained yielding a boundary following the relation: $P = 0.0075T + 2$ (kbar, °C). Measurements at room temperature suggest a very small volume change ($\Delta V/V_o = 0.0025$) at the transition. The data are in remarkable agreement with a recently proposed boundary between two hydration mechanisms in cordierite (Mirward *et al.*, 1979). Supporting evidence for the high-pressure transition is obtained from X-ray data on quenched samples of hydrous Mg-cordierite, which indicate no change in crystal symmetry but significant changes in the lattice parameters. Because up to 2 mol H_2O per formula unit have been determined in quenched high-pressure cordierite, a new hydration model is proposed involving a side by side accommodation of H_2O molecules in the channel cavities of the high-pressure phase. An appraisal of the thermodynamic quantities yields only small changes: $\Delta V = 0.6$ cm^3/mol and $\Delta S = 0.5$ J/mol K. The available observations suggest that this high-pressure transition in cordierite is likely to be of higher order.

Introduction

Cordierite, $(Mg, Fe)_2Al_4Si_5O_{18}\cdot nH_2O$, $0 \leq n < 2$), a common mineral in metapelitic rocks, has been attracting increasing mineralogical interest during recent years. Numerous experimental studies have focussed on its complex crystal-chemical behavior (*e.g.*, Schreyer and Schairer, 1961; Schreyer, 1965; Povondra and Langer, 1971). In particular, efforts have been made to elucidate the hydration of cordierite and its *P–T* stability (*cf.* Schreyer and Yoder, 1964; Seifert and Schreyer, 1970; Newton, 1972; Mirwald and Schreyer, 1977; Holdaway and Lee, 1977; Mirwald *et al.*, 1979; Lonker, 1981). In most of these studies Mg-cordierite served as starting material, since it is less difficult to synthesize and handle experimentally than Fe-containing solid-solution members.

Structural studies at ambient conditons on this framework silicate (Gibbs, 1966), in which channels enclosed by six-membered rings have a close relationship to the beryll structure (Gossner, 1928; Byström, 1942), are numerous (*e.g.*, Miyashiro, 1957; Smith and Schreyer, 1962; Goldman *et al.*, 1977; Wallace and Wenk, 1980). High-temperature data are also available (Hochella *et al.*, 1979). However no investigation has so far concerned itself with structural aspects at elevated *P–T* conditions. This report describes a high-pressure phase transition in cordierite studied with a volumetric technique. Preliminary data have been reported by Mirwald and Maresch (1980).

Method

High-pressure experiments were carried out with a conventional piston-cylinder high-pressure apparatus. For experiments at elevated temperatures a low-friction cell (Mirwald *et al.*, 1975) was used, allowing pressure release to 0.1 kbar without failure of the chromel-alumel thermocouple. Usually NaC1 was employed as the pressure-transmitting medium; above 800°C NaF was used. About 100 mg of sample material was sealed in gold capsules. Runs at room temperature were, however, conducted with larger samples (~3.5 g) wrapped in lead foil of 1 mm thickness. The design for this type of experiment is described by Vaidya and Kennedy (1970), while the basic volumetric technique was developed by Bridgman (1914). Essentially, pressure and piston-displacement are monitored at isothermal conditions. A strain gauge connected to the hydraulic system of the ram records the pressure with a resolution of 30 bars; piston displacement is moni-

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tored with an inductive transducer resolving displacements on the order of 10^{-5} cm. Both parameters are digitally monitored and simultaneously recorded on a strip chart recorder. A plot of pressure *versus* piston displacement (Fig. 1) yields the characteristic friction loop for solid-media pressure devices. Further details are given elsewhere (Mirwald, 1979).

The pressure accuracy in this dynamic experiment is estimated to be ±300 bars; the temperature stated is believed to be within ±10 degrees. The temperature error is greater than usually accepted, but more complete pressurization of the thermocouple wires enclosed in high strength alumina tubing and possible work hardening effects of the thermocouple associated with multiple cycling in a run (*cf.* Mirwald *et al.*, 1979) have to be taken into account.

For most experiments, synthetic anhydrous Mg-cordierite served as starting material. In addition, in one compression experiment at room temperature, natural cordierite from Soto, Argentina of intermediate composition, $Na_{0.03}(Mg_{1.2}Fe_{0.75}Mn_{0.05})Al_4Si_5O_{18}\cdot 0.4H_2O$ was used. Schreyer *et al.* (1979) give a detailed description of this material. The lattice parameters of the sample material are given in Table 2. The X-ray powder diffractometer data are based on an evaluation of 20 to 24 reflections between 20–70° 2θ, using Cu-radiation and Si as internal standard.

Results

While for natural Mg,Fe cordierite only one datum at room temperature has been obtained, isothermal compression experiments up to 900°C have been performed on synthetic anhydrous Mg-cordierite (Table 1). In Figure 1 the measurements for the Soto cordierite at room temperature and for Mg-cordierite at 730°C are displayed in a plot of pressure *vs.* piston displacement. In both graphs a break in the compression and decompression curve is evident, *e.g.*, at 2.1±0.3 kbar at 25°C and 7.8±0.3 kbar at 730°C. For the measurements at 730°C two pressure cycles (I, II) are given in order to show the reproducibility of this kind of volumetric technique. Similar discontinuities have been detected in runs at 510, 600 and 900°C (see Table 1). It is characteristic of these data that even at room temperature the discontinuities appear without hysteresis effects. There is a rather small pressure interval between the onset of the break at compression and the one at decompression.

These breaks are to be related to volume discon-

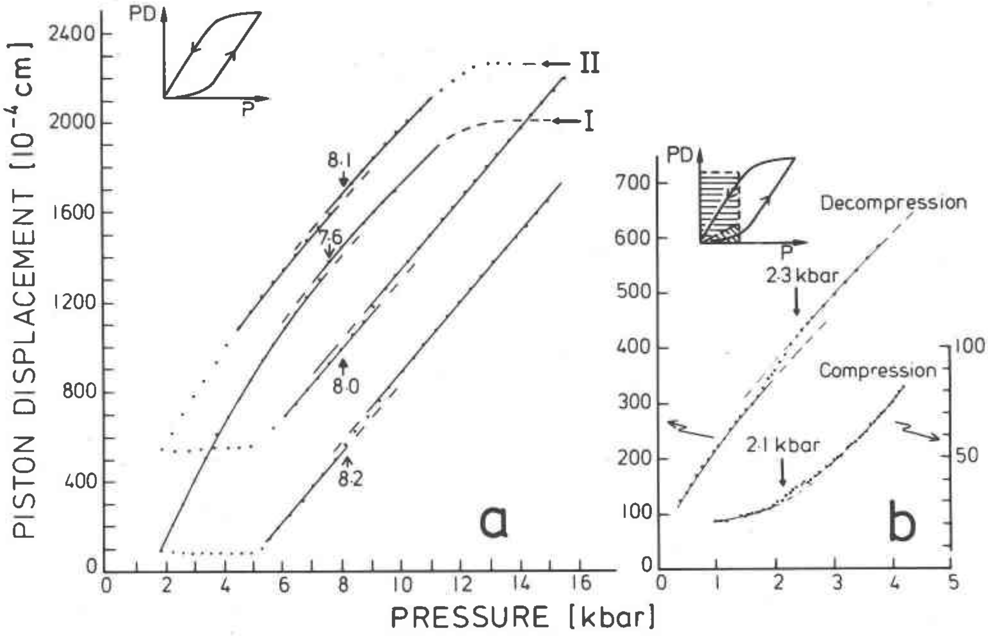

Fig. 1. Volume discontinuities exhibited by a) synthetic, anhydrous Mg cordierite at 7.8±0.3 kbar/730°C and b) natural, hydrous Mg,Fe cordierite (Soto/Argentina) at 2.2±0.3 kbar/25°C in compression experiments. The inserts in a) and b) give schematically the typical hysteresis ("friction") loop for solid-media pressure devices. The differently ruled regions of the insert in b) reflect the different scales used to depict the compression and decompression curves.

Table 1. Volume discontinuities of natural, hydrous Mg,Fe cordierite (Soto/Argentina) and synthetic, anhydrous Mg-cordierite at different *P–T* conditions.

Sample	Compression (Kbar)	Decompr. (Kbar)	P (Kbar)	T (°C)
Hydrous Mg,Fe cordierite (Soto)	2.1	2.3	2.2±0.1	25
Anhydrous Mg cordierite	1.8	2.0	1.9±0.2	25
		5.8	5.8±0.3	510±10
		6.3	6.3±0.3	600±10
	7.6 $^{+}$ 8.0 $^{++}$	7.6 $^{+}$ 8.1 $^{++}$	7.8±0.3	730±10
	8.6	8.95	8.8±0.3	900±10

$^{+}$first pressure cycle

$^{++}$second pressure cycle; cf. Fig. 1 b

tinuities encountered in the pressurized cell assembly. Since none of the pressure transmitting materials used displays volume discontinuities related to a phase transition in this *P–T* range, this discontinuous pressure and volume behavior must be attributed to the sample. To ensure that this effect is not related to apparatus behavior either, comparative compression runs were made at room temperature on powdered quartz (Dörentrup/Germany). No discontinuities were detected.

A straight line fit through the high-temperature data yields a d*P*/d*T* slope of some 7 bars/K (Fig. 2). Its extrapolation towards lower temperatures shows fair agreement with the two room temperature data. Because of the small sample and the additional presence of various pressure transmitting media required for a high-temperature pressure cell the high-temperature compression measurements are qualitative with respect to volume change. The larger sample masses in the room temperature experiments, however, allow estimation of the volume change of the transition from the offset in the decompression curve (Fig. 1b). (The break in the compression curve is difficult to evaluate due to its location in the lower portion of the friction loop, which is very insensitive in terms of piston displacement. This circumstance also required its display in Figure 1b at a more expanded scale.) For both cordierites a $\Delta V/V_0 \simeq -0.002$ was obtained.

In order to check for possible influences of pressure on the cordierite structure, powder diffractograms were prepared on the natural and synthetic sample after compression to 15 Kbars at room temperature. The lattice parameters obtained are

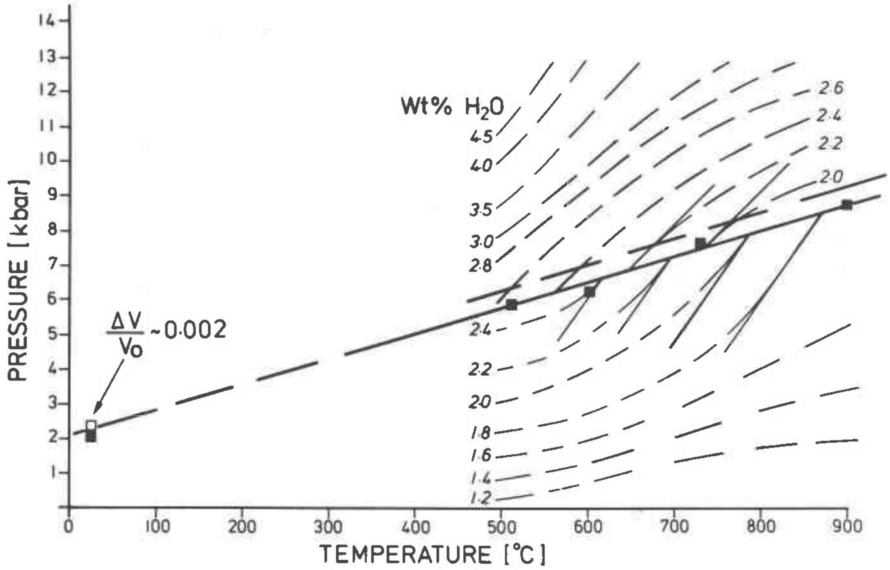

Fig. 2. Boundary of the high-pressure transition in cordierite between 25 and 900°C based on six data (solid squares: anhydrous Mg-cordierite, open square: hydrous Mg,Fe cordierite (Soto/Argentina). Thin dashed lines: H_2O isopleths (wt.%) of hydrous Mg-cordierite (slightly modified after Mirwald *et al.*, 1979) H_2O data are based on coulometric determinations. Thick dashed line: boundary of different hydration mechanisms as derived from H_2O content data by Mirwald *et al.* (1979). Thin lines: tangents to H_2O isopleths at the transition boundary.

compared with those of the starting materials in Table 2.

Table 2. Lattice parameters of synthetic, anhydrous Mg-cordierite and natural, hydrous Mg,Fe cordierite (Soto/Argentina).

	Anhydrous Mg cordierite		Hydrous Mg,Fe cordierite	
Parameter	starting material	after compression[++]	starting material	after compression
a[Å]	17.064(3)[+]	17.063(3)	17.125(1)	17.141(2)
b[Å]	9.721(2)	9.721(2)	9.753(1)	9.767(1)
c[Å]	9.340(3)	9.339(2)	9.326(1)	9.335(1)
V[$Å^3$]	1549.4(5)	1549.1(4)	1557.7(2)	1562.6(2)

[+] number in paranthesis represents 1σ associated with the last decimal immediately to the left

[++] to 15 Kbar at 25°C

Discussion

The volume discontinuities in Mg-cordierite observed at high pressure and varying temperatures are interpreted as a phase transition. The location of the phase boundary between 25 and 900°C is approximated by the relation:

$$P \simeq 0.0075T + 2, \text{ (kbar,°C)}.$$

The same interpretation is assumed for the natural cordierite of intermediate composition. Although no *in situ* data on the cordierite structure are available as yet, this suggestion may be supported by a number of additional observations and considerations.

First, the proposed phase boundary is in striking correspondence with observations derived from a study of the H_2O content of Mg-cordierite (Mirwald *et al.*, 1979). The H_2O data in that study, schematically represented by isopleths in Figure 2, had suggested two *P–T* regimes of different hydration mechanisms for Mg-cordierite. The estimated boundary between the two regimes proposed is given in Figure 2 by the thick dashed line. The *P–T* difference from 0.5 kbar and 75°K to the directly measured boundary is insignificant: thus it appears most likely that the two different hydration mechanisms are structurally controlled. This implies that the thermodynamic model on the hydration of cordierite derived by Newton and Wood (1979) from H_2O content data by Mirwald and Schreyer (1977) is inapplicable. Neither is the *PVT* behavior of cordierite continuous, nor can it be assumed that the hydration mechanisms in the two *P–T* regimes are the same, as inferred by these authors.

Further support for the proposed transition in cordierite is provided by X-ray data. While anhydrous Mg-cordierite subjected to 15 kbar pressure at room temperature shows no changes in its lattice parameters (see Table 2 and Fig. 3), a different behavior is exhibited by hydrous Mg-cordierite quenched from elevated *P–T* conditions. As Figure 3 indicates, two data groups may be distinguished: (1) samples obtained from below the transition boundary exhibit an almost constant cell volume; (2) samples quenched from the *P–T* regime of the high-pressure phase indicate a smaller volume ($\Delta V/V_o$ -0.001). That this is not due to the different H_2O content of the two sample groups but due to structural differences in the quenched products is indicated by the slightly opposed trends in the lattice parameters. In particular the *a* parameters of the high-pressure samples show, remarkably enough, a slight increase compared with low-pressure cordierite of comparable H_2O content. The latter observation will be discussed further below in context with structural considerations.

A main conclusion of the presented X-ray data is that a fluid channel component is apparently able to preserve relict features of structural states realized at elevated *P–T* conditions. This is an indirect confirmation of the results of the high-pressure experiments. In principle it is clear that similar behavior also should be expected for a more complex composition of the channel content with *e.g.*, additional CO_2, noble gases, alkali elements *etc.* as found in natural cordierites. However, a system of multicomponent channel volatiles probably could not be interpreted in such a straightforward manner (*cf.* Armbruster and Bloss, 1980).

Detailed structural analysis, such as an appraisal of the relative intensities of the diffractograms has not as yet been carried out. Similar analysis in an X-ray study on the location of argon and water in cordierite by Smith and Schreyer (1962) yielded no conclusive results. However, no differences in lattice parameters between anhydrous and hydrous Mg-cordierite were noticed then either. Possibly the relatively slow quenching rate in the gas pressure apparatus used in that study as compared to the present piston-cylinder pressure apparatus leads to nonequilibrium effects, as this was observed in hydration experiments at high-temperature by Mirwald *et al.* (1979).

Compressions and decompression of the Mg–Fe-cordierite from Soto gives different effects on the unit cell parameters than those observed for synthetic hydrous Mg-cordierite (Table 2). There may be two reasons for this: (1) the natural cordierite behaves differently from pure Mg-cordierite owing to its more complex chemistry (*cf.* Schreyer *et al.*, 1979), or (2) high-pressure cordierites depressurized at low temperatures may not be comparable in structural respects with cordierite quenched from elevated *P–T* conditions because of a further (high-temperature) transition in the high-pressure regime. If so, this might apply also to the data by Smith and Schreyer (1962). Comparative measurements on hydrous Mg-cordierite at room temperature have not yet been completed.

Structural considerations

The framework structure of cordierite belongs to space group Cccm (Gibbs, 1966; Cohen *et al.*, 1977). Except for one Si and one Al site the remaining ten sites of the cordierite structure occupy general positions in the unit cell and small continuous or discontinuous changes in the atomic parameters need not necessarily be accounted for by symmetry changes. It is interesting to speculate on the structural aspects of the proposed high-pressure transition on the basis of available evidence.

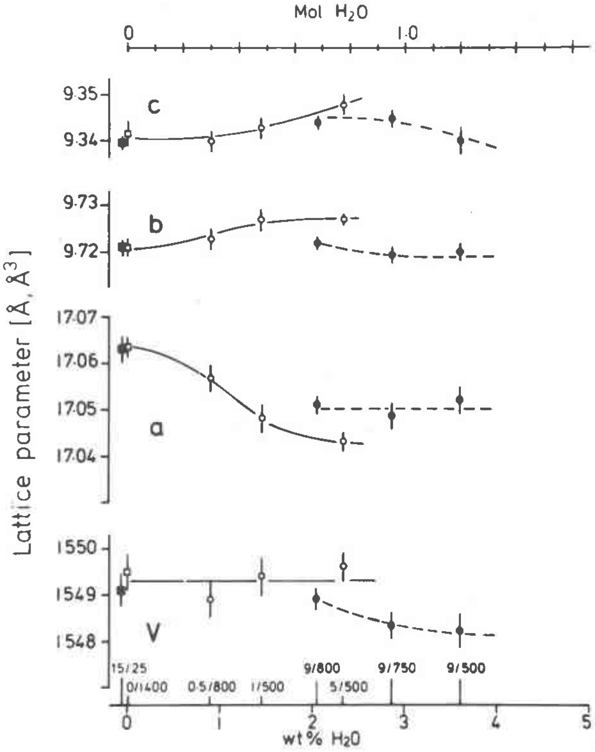

Fig. 3. Lattice parameters of quenched Mg-cordierite as a function of quenched H_2O content. Open square: anhydrous starting material prepared at 1400°C, solid square: anhydrous sample after compression to 15 kbar/25°C. Open circles: hydrous samples quenched from below the transition boundary, solid circles: hydrous samples from above (*P–T* conditions of equilibration are given above the abscissa in kbar, °C).

As pointed out, the X-ray data obtained from quenched hydrous Mg-cordierites give indirect support of structural changes at high pressures. The structure determination of Byström (1942) demonstrated that H_2O incorporated into cordierite is accommodated in the cavities of the channels formed between six-membered Si/AlO$_4$ tetrahedral rings stacked in the crystallographic *c* direction. With regard to the orientation of H_2O in the channel cavities, Farrell and Newham (1967) and Tsang and Ghose (1972) suggested that the H_2O molecules are oriented in the (100) plane with their H–H direction parallel to [001]. A second type of H_2O orientation with H–H direction in [010] has been reported for alkali-containing cordierites by Goldman *et al.* (1977). In infrared spectra, the specific bands at 1630 and 3574 cm^{-1} of the second type of H_2O orientation cannot be verified in the synthetic Mg-cordierite regardless of the *P–T* conditions of hydration below or above the proposed boundary. However, it has been found in the natural sample from Soto in our preliminary infrared absorption studies.

The H_2O content of high-pressure Mg-cordierite exceeds 3 wt.% or 1 mole H_2O per formula unit (*cf.* Mirwald *et al.*, 1979; Fig. 2). Recent unpublished experimental data indicate that up to 6 wt.% or 2 mole H_2O per formula unit can be contained in cordierite metastably. This implies that more than one molecule of H_2O can be accommodated per channel cavity. It seems difficult to accommodate 1 H_2O in the center of the six-membered rings for geometrical reasons (*cf.* Smith and Schreyer, 1962). Moreover, this would lead to stacking of H_2O molecules in the channel with attendant symmetry problems. A side by side accommodation of the H_2O molecules (diameter ~ 2.8Å) in the large cavities leads to a more favorable model. While, on the basis of geometry and dimensions of the cavity (*a* direction ~ 6Å, *b* direction ~ 5Å), this already seems possible for cordierite of the low-pressure form, such an arrangement should certainly be facilitated by a widening of the channel cavities as is indicated by the enlarged *a* parameter of hydrous Mg-cordierite quenched from the high-pressure regime (Fig. 3). This picture also seems consistent with preliminary data of a current X-ray diffraction study at high pressure, which confirms the behavior of the *a* parameter. These observations indicate that high-pressure cordierite exhibits a considerably anisotropy in compressibility. Taking, into account the above-mentioned high contents in H_2O, it also seems likely that the bulk compressibility of high-pressure cordierite is partly controlled by the compression behavior of the channel elements of the structure. With regard to the considerable H_2O content, a more zeolite-like character of the high-pressure form than for the low-pressure phase seems likely. This again raises the question of the nature of the interaction between H_2O and the host crystal, which cannot be answered at the moment.

Thermodynamic implications

From the present compression data at room temperature and the previously reported H_2O content data (Mirwald *et al.*, 1979) a rough estimate of the thermodynamic quantities involved in the transition can be derived. Assuming as a first estimate that the phase transition is first order, the dP/dT slope of ~7.5 bar/K given above and the measured $\Delta V/V_o$ of -0.6 cm^3/mol yield according to the Clausius–Clapeyron relation, a change in entropy at the transition of $\Delta S \sim 0.4$ J/mol·K. These quantities are relatively small and of comparable order of magnitude as for example those of the low/high quartz inversion.

Speculations on the order of the transition

From the data presented it is not evident whether this observed volume discontinuity is due to an abrupt change in specific volume of cordierite (*e.g.* $\Delta V < 0$ and $dV/dP < 0$) or is caused by a rapid change in compressibility (*e.g.*, $\Delta V = 0$ but $dV/dP < 0$). Inherent experimental limitations, such as friction effects, may also play a role. The very small magnitude of this volume change seems to favor the assumption of a nonreconstructive phase transition. This might explain why no structurally different polymorphs of cordierite have been found, except for the hexagonal high-temperature form "high-cordierite" (indialite). On the other hand, as pointed out above, small changes in the atomic parameters do not necessarily alter the symmetry of the cordierite structure. This leads to the possibility of a displacive character of the high-pressure transition. A diffusive transition mechanism operating at low temperatures seems very unlikely. Finally, the striking observation that even at room temperature no pronounced pressure hysteresis at the transition could be identified implies that this high-pressure transition in cordierite may be of higher order. There are various kinds of higher-order transitions. This one must at least be discontinuous in compressibility and thermal expansion as this is indicated by the offset of the H_2O isopleths across the transition boundary.

Acknowledgments

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