

## X-ray powder-diffraction and infrared study of the hexagonal to orthorhombic phase transition in K-bearing cordierite

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### ABSTRACT

The phase transition in annealed samples of K-bearing cordierite ( $K_{0.2}Mg_2[Al_{4.2}Si_{4.8}O_{18}]$ ) from the hexagonal form to the modulated form to the orthorhombic form has been studied by hard-mode infrared spectroscopy and by synchrotron X-ray powder diffraction. Our results reveal the behavior of (Al,Si) ordering ( $Q_{od}$ ) and spontaneous strain or orthorhombic distortion ( $Q$ ) as a function of annealing time during this time-dependent transition. Two phase transitions are observed, namely between a hexagonal and a modulated form and between a modulated and an orthorhombic form. Both transitions are strongly first order. The structural states of K-bearing cordierite appear to be very similar to the pure-Mg cordierite with the following modifications: (1) The maximum distortion of the orthorhombic structure leads to a strain corresponding to a  $\Delta$  index of  $\Delta = 0.17$  as compared to  $\Delta = 0.25$  in pure-Mg cordierite. (2) The kinetics of the transformation process are accelerated by a factor of about two by doping with K. A thermodynamic description of the transition behavior leads to a form for the Landau potential in which the effect of K in the structure is identified as a strain field conjugate to the order parameter.

### INTRODUCTION

Pure-Mg cordierite,  $Mg_2Al_4Si_5O_{18}$ , is orthorhombic (space group *Cccm*) under equilibrium conditions below about 1450 °C; a hexagonal polymorph (space group *P6/mcc*) is stable above this temperature (Schreyer and Schairer, 1961; Putnis, 1980). The transition between these two structures is associated with changes in (Al,Si) order: the hexagonal form cannot accommodate any long-range order of the Al and Si atoms, whereas the orthorhombic form can attain complete order of atoms on the Al and Si sites. The study of the temperature-dependent equilibrium behavior of cordierite around this phase transition is experimentally difficult because of the high temperatures involved. Annealing experiments on glasses of cordierite composition have, however, revealed that the same phases evolve as a function of time (Schreyer and Schairer, 1961). This kinetic approach has been used to shed light on the possible equilibrium behavior of cordierite. It is found that the first cordierite phase to crystallize from the glass is hexagonal, and further annealing leads to the development of a modulated structure, which in turn transforms to the true low-temperature equilibrium phase, which has orthorhombic symmetry (Putnis et al., 1987; Salje, 1987; Güttler et al., 1989).

Natural cordierites invariably accommodate additional elements within the structure (for a recent summary, see Schreyer, 1985). In most cases, H<sub>2</sub>O molecules are present in the large channels that run parallel to the *z* axis, which often contain Na and occasionally K. For this reason it was decided to investigate the influence of the presence of K on the structural phase transition in cordierite. Here we present the results of a study of the hexagonal to orthorhombic phase transition in a synthetic cordierite of the composition  $K_{0.2}Mg_2[Al_{4.2}Si_{4.8}O_{18}]$ . The addition of K directly affects the (Al,Si) ordering behavior, since the substitution of K + Al for  $\square$  + Si that operates here necessarily alters the Al:Si ratio from that in pure-Mg cordierite. The phase transition is triggered by a critical degree of (Al,Si) order ( $Q_{od}$ ), which causes a sudden distortion of the structure that breaks the hexagonal symmetry and leads to the orthorhombic structure (the spontaneous strain, proportional to a long-range order parameter  $Q$ ; for details see Salje, 1987). Additional effects may be introduced by local strains due to the incorporation of K. The local stress field associated with such a point defect (in this case a K atom in a channel) may act as the conjugate field to  $Q$  and alter the phase-transition behavior and character.

This paper uses the techniques and theory developed earlier to describe the transition behavior of pure-Mg cor-

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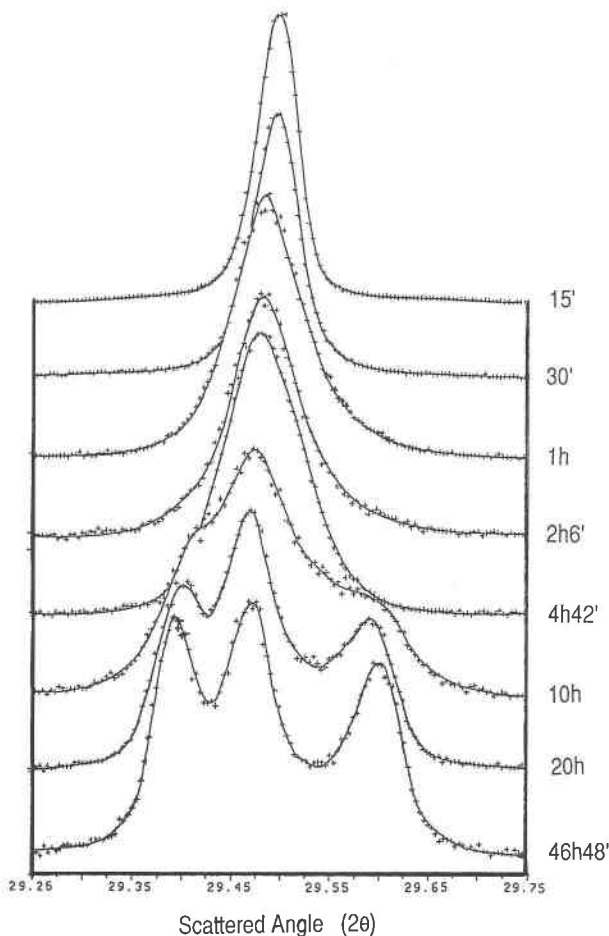


Fig. 1. Synchrotron X-ray diffraction profiles of a suite of annealed samples showing the splitting of the (211) hexagonal peak (top) to the (511), (421), and (131) peaks of the orthorhombic phase.

dierite (Salje, 1987), but addresses the influences of additional channel-filling K and hence changed Al:Si ratio on the transition. Both the orthorhombic long-range distortion and the local distortions have been studied as a function of annealing time in a suite of K-bearing cordierites.

#### EXPERIMENTAL DETAILS

The samples used for this study were prepared from cordierite glass of the given stoichiometric composition as described by Wolfsdorff (1983). A suite of crystalline specimens was obtained by annealing the glass in air at 1290 °C for varying times before quenching. Samples annealed for 15 min, 30 min, 1 h, 2 h 6 min, 4 h 42 min, 10 h, 20 h, and 46 h 48 min were selected for infrared and synchrotron X-ray investigation.

#### Synchrotron X-ray powder diffraction

The cordierite samples weighing around 20 mg each were ground by hand in an agate mortar and loaded into

quartz-glass capillaries of 0.3-mm internal diameter. These capillary samples were mounted in Debye-Scherrer geometry on a spinning goniometer head on the high-resolution Stoe 2-circle diffractometer at station 9.1 of the synchrotron radiation source, Daresbury, England. The spinning frequency was 5 Hz, and the rotation axis of the samples was carefully aligned to coincide with the  $2\theta$  axis of the diffractometer. The advantage of this experimental arrangement over other possible diffraction experiments is that the instrumental line profile may be fitted by a simple peak function. Our measurements of hexagonal cordierite yielded a 211 peak that was fitted by a general Voigt profile and found to be 95% Gaussian. In addition the high-incident beam flux obtained leads to an excellent signal-to-background ratio, as can be seen from the experimental results (Fig. 1). The long  $2\theta$  arm (specimen to detector distance = 650 mm) and high mechanical stability of the instrument at station 9.1 lead to a very good angular resolution, allowing attainment of line widths (FWHM) as small as  $0.03^\circ 2\theta$  (also dependent on sample characteristics). This compares with a typical minimum FWHM of around  $0.07^\circ 2\theta$  on conventional X-ray powder diffractometers and means that the instrumental line function at the synchrotron may reasonably be assumed to be a delta function (thus avoiding the need to consider instrumental convolution effects). These features make this powder diffractometer ideally suited for the study of relative changes in line profiles and peak broadening and splitting. In particular, the experimental determination of small orthorhombic lattice distortions in cordierite requires the high-resolution diffraction data typically obtainable at a synchrotron source.

Synchrotron radiation was monochromated using a He-filled Si (111) channel-cut monochromator, and monochromatic radiation of wavelength 1.5406 Å was used for all measurements. The wavelength was calibrated both from the monochromator angle and from the position of the (111) peak of high-purity Si, which was present in all samples as an internal standard. Since there was no need for energy-dispersive measurement, a scintillation counter was employed as the detector. The monitored incident-beam intensity was stable to within 0.2% during the period of our measurements. The diffraction experiments were performed at room temperature over a range of  $29.25^\circ$  to  $29.75^\circ 2\theta$  by step scan with a step size of  $0.002^\circ 2\theta$  and a counting time of 5 s per step.

#### Hard-mode infrared measurements

Infrared spectra of the powdered cordierite samples were obtained using a standard KBr pellet technique. All samples were prepared in a similar fashion: milled for 30 min in a Spex micromill and mixed with dry KBr in a ratio of 1:300 sample to KBr. Each pellet weighed 200 mg and was pressed under vacuum to give optically transparent pellets. Great care was taken to ensure, as nearly as possible, identical conditions for the preparation of each sample pellet.

The spectra were recorded at room temperature under vacuum on a Bruker 113v Fourier-transform infrared spectrometer. Spectra were measured in the range 1400 to 400  $\text{cm}^{-1}$  and in each case were calculated from 512 sample scans using an Aspect 3000 computer. Band-profile analysis was carried out on the same computer, fitting Voigt profiles to the measured spectra by least-squares refinement. The maximum  $R$  factor of the fitting procedure was 0.03%, giving errors of  $\pm 0.2 \text{ cm}^{-1}$  in the line-widths (FWHM) and around 10% for the computed integrated intensities. The absolute frequency of the absorption bands was obtained to a similar accuracy of  $\pm 0.2 \text{ cm}^{-1}$ .

The use of hard-mode infrared spectroscopy (HMIS) in this study follows the same lines as that of Güttler et al. (1989). In this approach the absolute values of absorption frequency are dependent upon sample characteristics, but the structural effects of the phase transition are characterized by *relative* changes in band frequencies, intensities, and half-widths.

## RESULTS

### Strain behavior from diffractometry

The traditional method of observing the structural distortion of the cordierite unit cell resulting from the hexagonal to orthorhombic transition relates to the splitting of the hexagonal (211) diffraction peak. This splits into the (131), (421) and (511) peaks in the orthorhombic structure. Miyashiro (1957) first drew attention to this splitting as a means of measuring changes in structural order through the phase transition when he defined the distortion index,  $\Delta$ , which is proportional to the peak splitting in the orthorhombic phase. This distortion index results directly from the spontaneous strain at the phase transition and is proportional to the long-range displacive-order parameter,  $Q$ , of the transition. Putnis et al. (1987) related the index,  $\Delta$ , directly to  $Q$  for the case of pure-Mg cordierite and found that in this case  $Q \approx 4\Delta$  for  $\Delta$  measured with Cu radiation. We used a similar approach for the investigation of the samples described here and observed the macroscopic strain behavior of K-bearing cordierites by careful measurement of the evolution of the (211) hexagonal peak through the suite of annealed samples.

The observed diffraction patterns between 29.25 and 29.75°  $2\theta$  are shown in Figure 1. At the shortest annealing time, the hexagonal (211) peak is sharp and intense (peak intensity of 25000 cps) and near-Gaussian (by fit to Voigt profile). With longer annealing, the (211) peak becomes noticeably and significantly broadened. This broadening corresponds to the development of a modulated phase, analogous with that observed in pure-Mg cordierite (Putnis et al., 1987). The width of the (211) peak corresponding to the modulated phase remains constant upon further annealing.

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ison (manuscript in preparation) have pointed out that the asymmetric diffuse scattering around the (211) peak consists of a composite of several satellite reflections associated with the modulated phase (compare Fig. 1,  $t = 4 \text{ h } 42 \text{ min}$ ). They assumed a distinct modulation wavevector and were able to fit 12 predicted satellite reflections to the asymmetric peak profile of modulated pure-Mg cordierite (data of Putnis et al., 1987, also obtained at station 9.1, SRS, Daresbury). An alternative interpretation is that the satellites are themselves diffuse and arise from a range of modulation wavelengths rather than from a single distinct wavevector, as suggested by Putnis et al. (1987). It is not possible to sensibly differentiate between these two scenarios in the light of the evidence from existing scattering experiments alone, and attempts to measure satellite intensities by TEM have proved unsuccessful. The number of free parameters for a fit of so many satellite reflections, which may themselves be composite, to one peak profile from powder diffraction is too great to allow a unique conclusion to be drawn.

The modulated phase appears as a precursor to the orthorhombic structure of K-bearing cordierite during the course of a kinetic experiment. The orthorhombic phase is identified in the X-ray scattering experiments here by the three distinct peaks that are apparent in samples annealed for 10 h or more (Fig. 1). As has been seen in pure-Mg cordierite (Putnis et al., 1987), when the orthorhombic phase first appears, it is already almost totally distorted with respect to the hexagonal cell. The orthorhombic cordierite obtained at the longest annealing time is not much more distorted. The distortion index in K-bearing cordierites does not change continuously with annealing, but undergoes a sudden discontinuity from zero to 0.155 on the transformation from modulated to orthorhombic cordierite (as observed on the length scale of X-ray experiments). Since the transition from modulated to orthorhombic is first-order, we expect a limited regime of coexistence of phases. This is observed in the spectra of the sample annealed for 10 h shown in Figure 1.

The distortion indices of the K-bearing cordierites measured here show a maximum value of  $\Delta = 0.17$ . This is significantly less than the maximum distortion index measured in pure-Mg cordierite of 0.25 (Putnis et al., 1987). The minimum nonzero value of the distortion index measured in this suite of samples is 0.155, whereas it is 0.22 in pure-Mg cordierite (Putnis et al., 1987). The measured  $\Delta$  indices for the three orthorhombic K-bearing cordierites we have studied are 0.155 (10 h), 0.16 (20 h), and 0.17 (46 h 48 min). Hence the structural distortion in K-bearing cordierites is always less than in orthorhombic pure-Mg cordierite samples. The behavior, however, follows the same trends in both sets of samples. In K-bearing cordierite, the distortion index changes discontinuously at some annealing time between 4 and 10 h. The large discontinuity in distortion index suggests a nucleation and growth mechanism for the formation of orthorhombic K-bearing cordierite from the modulated phase, as in pure-Mg cordierite.

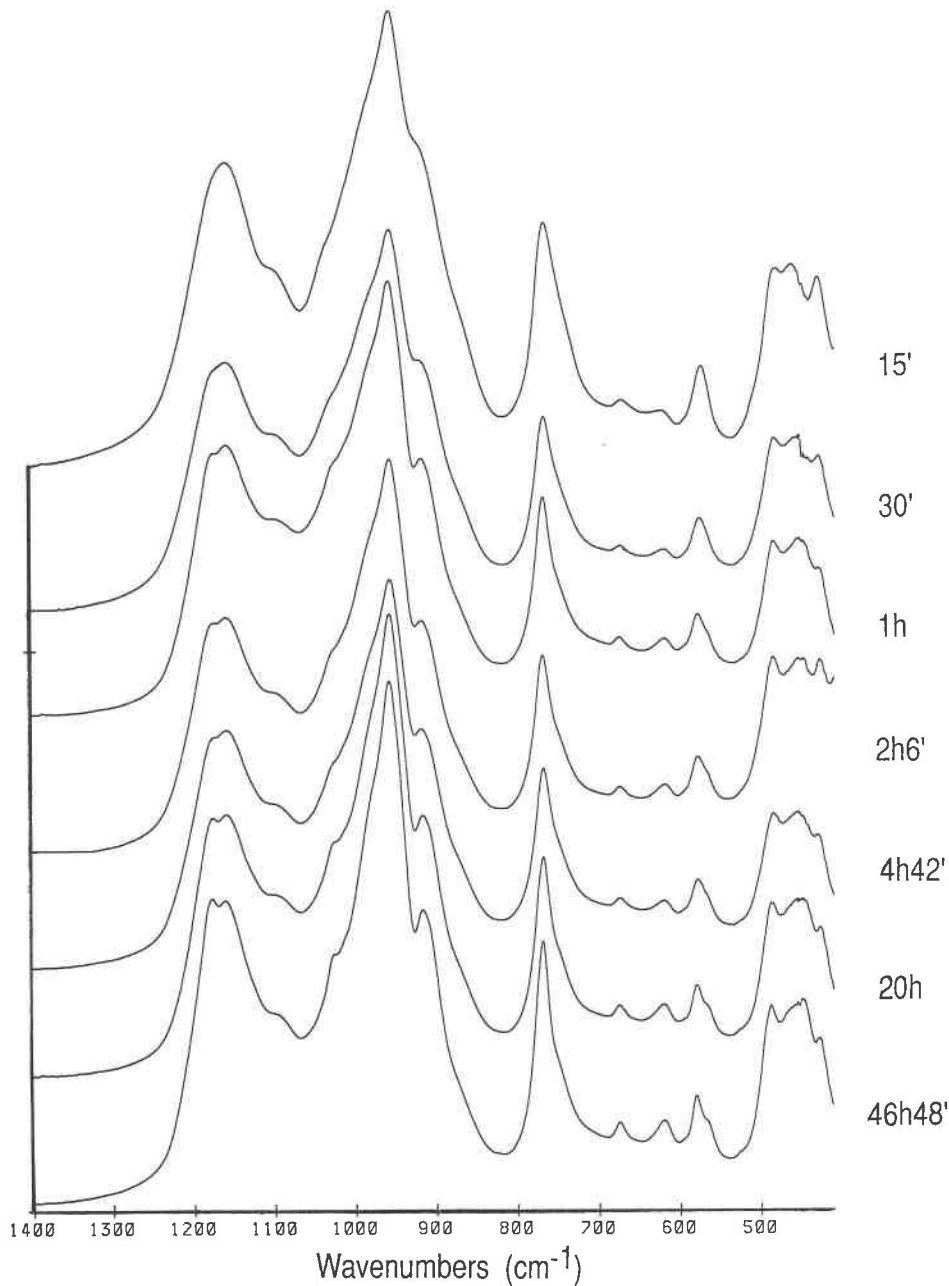


Fig. 2. Infrared spectra of annealed synthetic K-bearing cordierites.

#### Hard-mode infrared spectroscopy

Infrared spectra of the suite of annealed K-bearing cordierites are shown in Figure 2. Additional bands appear with increasing annealing time; among others they include one on the high-energy side of the  $580\text{ cm}^{-1}$  mode. The results from line-profile analysis of this band are shown in Figure 3. The fit shown represents the best agreement with the measured data using the minimum necessary component bands. The fit of all spectra was identical; in the case where the mode intensity of the

band near  $566\text{ cm}^{-1}$  could be fitted as zero, it was omitted from the spectrum fit. Splitting of the  $580\text{ cm}^{-1}$  mode is clearly seen in samples annealed for longer than 15 min. This splitting results directly from changing selection rules on the structural phase transition from the high-symmetry  $P6/mcc$  hexagonal phase to a phase with orthorhombic symmetry (space group  $Cccm$ ). No further splitting or additional bands are observed with longer annealing. These results are in essential agreement with the results of earlier studies by Langer and Schreyer (1969) and Güttler et al. (1989).

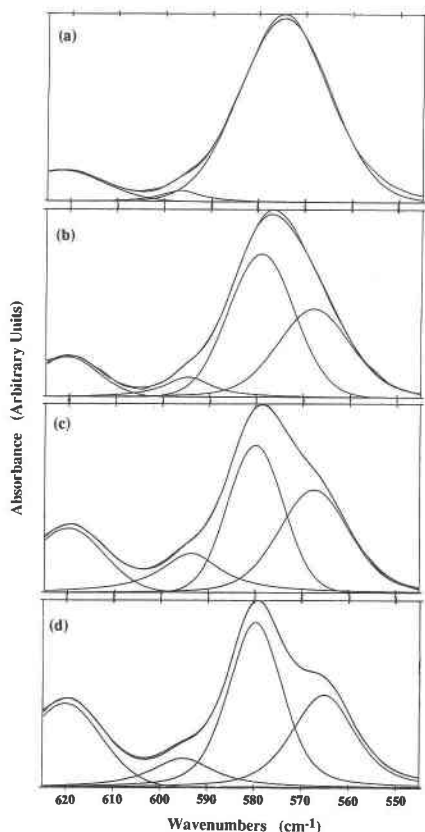


Fig. 3. Results of band-profile analysis of K-bearing cordierite crystallized from glass and annealed for (a) 15 min, (b) 30 min, (c) 1 h, and (d) 46 h 48 min.

The intensity of the additional side band at  $566\text{ cm}^{-1}$  is shown as a function of annealing time in Figure 4. We see a stepwise increase in intensity of this band, which does not change after 30 min. Thus, the hexagonal K-bearing cordierite must have changed before this time to the modulated state with orthorhombic symmetry on the length scale probed by the  $580\text{ cm}^{-1}$  mode. We have already seen that on the length scale probed by X-ray diffraction, the samples at these shorter annealing times (up to 4 h) appear hexagonal or modulated. In this respect, the behavior of this suite of samples is identical to that observed for pure-Mg cordierite. The stepwise transition from hexagonal to modulated cordierite (at the same local length scale) is underlined by the behavior of the peak frequency of the  $770\text{ cm}^{-1}$  band, shown in Figure 5.

### DISCUSSION

The experimental observations outlined above may be interpreted within the framework of a Landau model for the free energy of cordierite (Salje, 1987). The Landau model has recently been successfully applied to a number of phase transitions in minerals and works particular well for displacive transitions in crystals with a framework

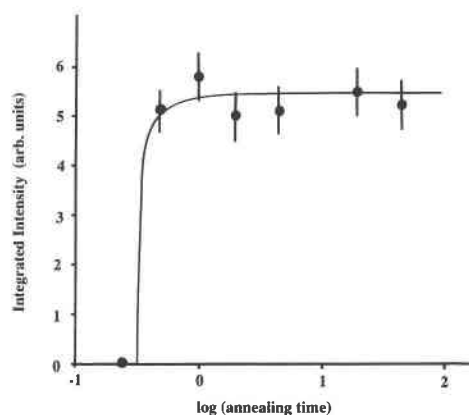


Fig. 4. Time evolution of the integrated intensity of the infrared mode near  $566\text{ cm}^{-1}$  in K-bearing cordierite.

structure (Redfern et al., 1988; Redfern and Salje, 1988). Cordierite may also be regarded as a framework silicate inasmuch as each  $\text{SiO}_4$  or  $\text{AlO}_4$  tetrahedron is connected to four others. The Landau model describes the stability of the orthorhombic form of cordierite in terms of the degree of (Al,Si) order on the tetrahedral sites ( $Q_{od}$ ), the distortion of the lattice away from hexagonal symmetry (the spontaneous strain), and the influence of channel-filling cations such as K. All of these structural features influence one another and couple to each other through the strain that arises in the structure as the lattice relaxes in response to them, and they may all be incorporated into one expression for the excess free energy of the orthorhombic phase with respect to the hexagonal phase.

The orthorhombic distortion (which is traditionally measured by the  $\Delta$  index) is expressed in the Landau expansion in terms of a displacive order parameter,  $Q$ , which is zero when  $\Delta = 0$  and increases in the same way as  $\Delta$  with time in the annealing experiments. The order parameter  $Q_{od}$  describes the degree of (Al,Si) order.  $Q_{od}$

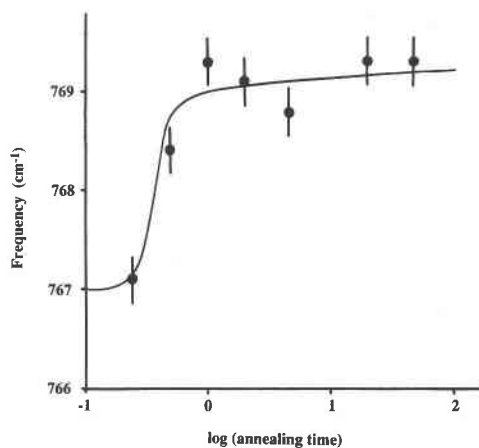


Fig. 5. Frequency shift of the infrared mode near  $770\text{ cm}^{-1}$  shown as a function of the logarithm of the annealing time for the suite of K-bearing cordierite glasses.

should be zero in the totally disordered hexagonal phase. The structure can, however, accommodate degrees of (Al,Si) order as large as  $Q_{od} = 0.8$  and still remain hexagonal, at least on the correlation length of X-ray diffraction (Putnis et al., 1987). Both  $Q$  and  $Q_{od}$  correspond to two-dimensional active representations in the point group of the high-temperature hexagonal symmetry and must themselves, therefore, be two-dimensional order parameters with components  $q_1$  and  $q_2$ , and  $q_{od,1}$  and  $q_{od,2}$  respectively. In addition, each order parameter may be defined on a local length scale as well as a macroscopic length scale. X-ray diffraction experiments would, for instance, probe the order parameters on a long length scale (a few hundred Å), whereas Raman and infrared experiments can shed light on the behavior of order on a local scale (a few tens of Å). The relationships between these order parameters and the possible point-group symmetries of cordierite are tabulated by Güttler et al. (1989).

It is now possible to formulate the Landau potential for pure-Mg (no K) orthorhombic cordierite, ignoring local monoclinic modulations (which are represented by  $q_2$ ). Following the approach of Salje (1987), we write this as an excess free energy:

$$\Delta G(Q_{od}, q_1) = \frac{1}{2}a_{od}^*Q_{od}^2 + \frac{1}{3}b_{od}Q_{od}^3 + \frac{1}{4}c_{od}Q_{od}^4 + \frac{1}{2}aq_1^2 + \frac{1}{3}bq_1^3 + \frac{1}{4}cq_1^4 + \lambda Q_{od}q_1, \quad (1)$$

where  $a_{od}^*$ ,  $b_{od}$ ,  $c_{od}$ ,  $a$ ,  $b$ , and  $c$  are the normal Landau coefficients for the expansion containing a cubic term and including fourth order terms. The last term in this expansion results from bilinear coupling (Salje and Deva- rajan, 1986) between  $q_1$  and  $Q_{od}$  that operates at the hexagonal to orthorhombic transition in cordierite, and  $\lambda$  is the coupling constant. Equation 1 predicts the first-order behavior and formation of a modulated phase during annealing of originally hexagonal cordierite.

Our experimental results indicate that the structural states of the K-bearing samples are essentially the same as in pure-Mg cordierite. The two essential differences are first, that the highest degree of (Al,Si) order is lower than in the K-free material (i.e., the maximum value of  $Q_{od}$  is less than unity) and, second, that the maximum spontaneous strain is also reduced from a distortion index of 0.25 to 0.17. There are experimental indications that phase mixtures of coexisting cordierites occur over limited periods of annealing time. The 10-h sample shows modulated and orthorhombic cordierite in coexistence, and the peak intensities of the diffraction pattern of the 20-h sample may also be interpreted in terms of a similar phase mixture. It should be borne in mind, however, that inhomogeneity in K distribution and grain size would also lead to line broadening, which could account for the diffraction profile of the 20-h sample. Whatever the extent of coexistence actually is, the results seem to imply that the effect of doping with K cannot simply be described as local defect perturbations within the cordierite lattice, as in the Ornstein-Zernicke formalism (Levanyuk et al., 1979; Salje, 1987, 1988; Strukov et al., 1980). Rather, it

appears that the defect concentration is high enough that the effect of the combined local stress fields of all the individual K atoms may be thought of as a homogeneous field (as opposed to a purely local field). This is convenient since this homogeneous stress field due to the K defects may then be treated in the Landau formalism of cordierite as a conjugate field to the order parameter. In this case, we can rewrite the Landau potential of Equation 1 as

$$\Delta G(Q_{od}, q_1) = \frac{1}{2}a_{od}^*Q_{od}^2 + \frac{1}{3}b_{od}Q_{od}^3 + \frac{1}{4}c_{od}Q_{od}^4 + \frac{1}{2}aq_1^2 + \frac{1}{3}bq_1^3 + \frac{1}{4}cq_1^4 + \lambda Q_{od}q_1 + HQ_{od} + hq_1 + \frac{1}{2}g_{od}(\nabla Q_{od})^2 + \frac{1}{2}g(\nabla q_1)^2. \quad (2)$$

The last four terms represent the proposed coupling with the conjugate fields  $H$  (conjugate to  $Q_{od}$ ) and  $h$  (conjugate to  $q_1$ ) due to incorporation of K and the fluctuational Ginzburg terms. The relative stabilities and kinetic behavior of cordierite depend on the homogeneity of  $H$  and  $h$ . In the treatment presented here, we have assumed  $H$  and  $h$  to be homogeneous fields opposing  $Q_{od}$  and  $q_1$  [hence the addition of K results in reduced (Al,Si) order and  $\Delta$  index in the orthorhombic phase, compared to those values observed in pure-Mg cordierite]. In addition, however, spatial variation of these fields might lead to relative stabilization of the modulated form, as has been pointed out by Michel (1984). The interval of annealing times over which modulated cordierite is found is expected to increase for K-bearing samples with respect to pure-Mg cordierite (Salje, 1987). Quantitative assessment of the kinetic behavior requires the experimental determination of  $H$  and  $h$ . Indirect evidence for the strength of  $H$  is still to be obtained from NMR spectroscopy, which could be used to determine the maximum degree of (Al,Si) order in K-bearing cordierite, allowing the calculation of  $H$  in the limit of homogeneous fields. It is, nonetheless, apparent that the introduction of defects such as K within the cordierite structure has a significant influence on the stability and kinetic behavior of cordierite. This is a general feature of phase transitions when the defect stress field acts as the conjugate field to the order parameter.

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