

**THERMAL EXPANSION BEHAVIOR OF DISORDERED AND ORDERED  
(NA)-MG-CORDIERITE BETWEEN 25 AND 700°C – A HIGH RESOLUTION XRD STUDY**

by

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Cordierite ( $[\text{Mg, Fe}]_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot n[\text{Na, H}_2\text{O, CO}_2, \text{etc.}]_{\text{channel}}$ , a framework silicate with characteristic channel elements, is an interesting mineral phase in granulitic metapelites and applied ceramics as well. Besides variable Mg/Fe ratios, sodium which is accommodated in the centre of the channel forming six membered ring elements, may be incorporated up to 0.6 mol% (WOLFSDORF & SCHREYER, 1992; MIRWALD, 1999).

Cordierite occurs in two structural modifications, high and low temperature cordierite. In nature the orthorhombic low temperature form prevails which is with respect to its Si-Al distribution ordered. In ceramics where cordierite is produced as polycrystalline material for numerous applications, it is of hexagonal symmetry being characterised by Si-Al disorder.

With respect to its physical properties the low thermal expansion behaviour of cordierite is very striking. Most studies have been performed on synthetic material (e.g. IKAWA et al., 1986). Measurements on natural material are rare (HOCELLA et al., 1979; ARMBRUSTER, 1986; SCHNEIDER & MIRWALD, 1999) due to the fact that fluid compounds in the structural channels as well as complex chemical compositions (MIRWALD, 1998) impair to reproducible conditions.

A reinvestigation of the thermal expansion on Mg-cordierite by X-ray powder diffractometry has been conducted between 25 - 700°C at 1 atm. The major goal was to study the influence of variable sodium content on its thermal behaviour, in particular with respect to the recently established thermal discontinuities (SCHNEIDER et al., 2001; MIRWALD, 1999) at some 250 - 300 and 500 - 600°C.

The material has been prepared from oxide mixes (cf. WOLFSDORFF & SCHREYER, 1992). Pure cordierite (indialite) was used from BAM (PEPLINSKI et al., 2000). For the thermal expansion measurements a Siemens D-5005 diffractometer (parallel beam optics, scintillation counter, Cu-target, 40kV, 40mA, 0.02 steps, 4 sec measuring time per step, 8 - 100 degrees  $\theta/2\theta$ ) equipped with a Paar HTK 1200 high temperature device (heating ramp 0.2°/sec in 10°C intervals from 20°C to 700°C) was used. Data evaluation have been done by using the Rietveld-algorithm implemented in TOPAS 2.0 (Bruker AXS).

In Fig. 1 a data compilation of the system synthetic Mg-cord. – NaMg-cord. is given – including our samples – relating the sodium content of Mg-cordierite by the elementary cell volume at some 25°C. Our samples cover the whole range of miscibility. Five compositions have been prepared (9, 15, 33, 53 and 55 mol%). After crystallisation from the glass all samples crystallised in the hexagonal high temperature form. Only the sodium free sample could be transformed into the rhombic low temperature form by heating at 1400°C for 20 days; the sample of 9 mol% Na-content turned out to be structurally and chemically inhomogeneous. In a first measurement campaign detailed thermal expansion measurements have been done on the chemical endmembers, hexagonal and rhombic 0.00 NaMg-cordierite as well as on hexagonal 0.60 NaMg-cordierite.

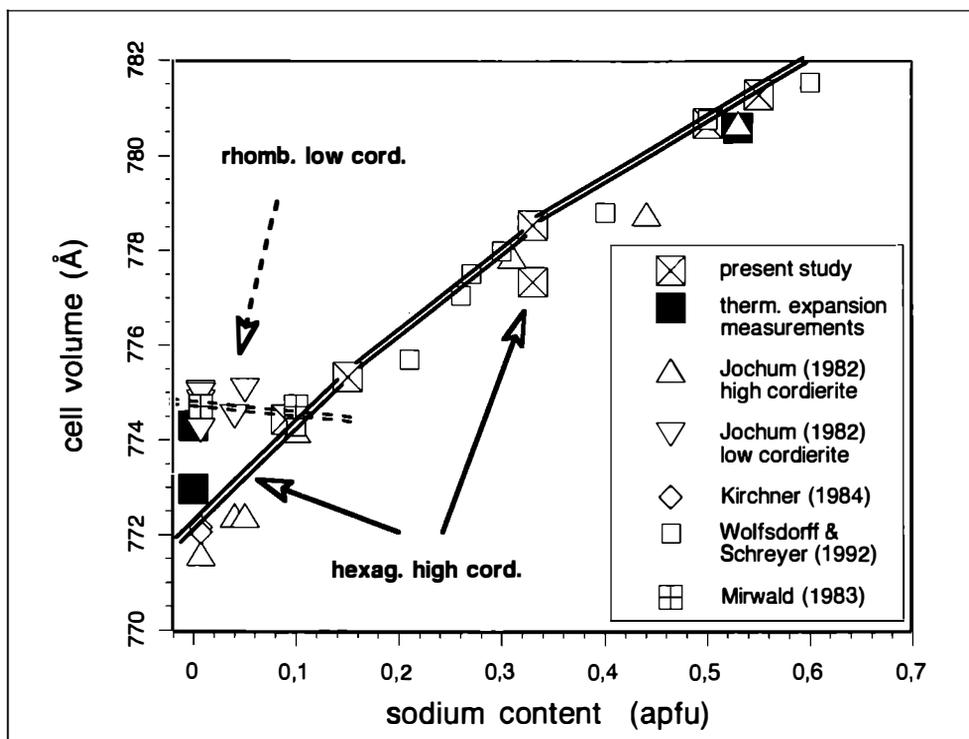


Fig. 1  
Plot of sodium content vs. cell volume compiled from different sources.

In a general way the data confirm the previous studies: small positive thermal expansion for the basis parameters and a negative expansivity for the c-parameter. However, detailed analysis of the three data sets reveals that the expansion behaviour is specifically different with respect to structural state as well as to the sodium content in the low temperature region up to 300°C (Fig. 2). In addition, the course of expanding volume curves show an irregular slope behaviour in the temperature region at 250 - 300°C and 550 - 600°C which is in relation to the sodium content of the samples. For comparison with the present data the volume expansion of White Well cordierite is also given in Fig. 2.

SCHNEIDER et al. (2001) recently have found a structural discontinuity in the temperature range 250 - 300°C. This discontinuity appears as a subtle kink in the lattice parameters, specially in the c-parameter, and is accompanied with a intensity jump of reflection peaks. A further discontinuity seems to be at 500 - 600°C. Both discontinuities are indicated in Fig. 2.

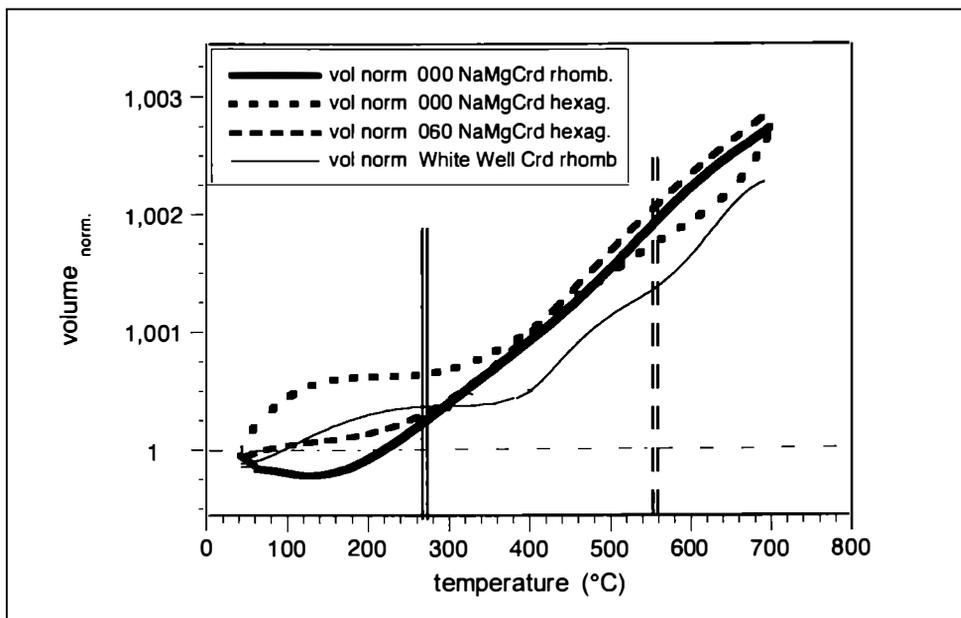


Fig. 2  
Temperature vs. cell volume (normalization: 25°C).

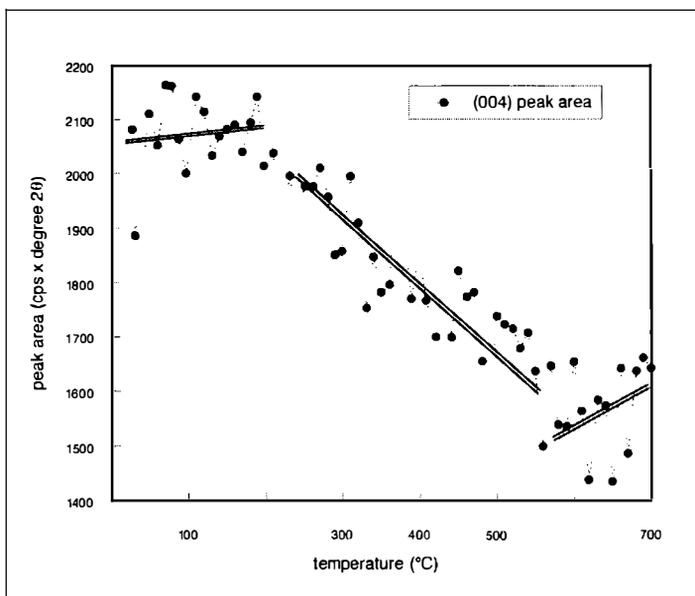


Fig. 3  
Temperature vs. peak area of the (004)-reflection of low cordierite ordered from high 000 NaMg-cordierite (indialite).

A comparable situation is encountered in the present data. While the cell parameters show only an indication of a kink, the change in intensity of the reflections is quite obvious as demonstrated by the peak area of the (004) reflection of the orthorhombic 000 NaMg-cordierite in dependence of temperature in Fig. 3.

These findings confirm previous work (MIRWALD, 1981, SCHNEIDER, TESSADRI & MIRWALD, 2001). They are supported by results obtained in electrical conductivity measurements (SCHMIDBAUER & MIRWALD, 1988a,b)) as well as by the H<sub>2</sub>O incorporation behaviour as reflected by changing slopes of the isohydrans (MIRWALD et al., 1979).

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