High-pressure phases of cordierite from single-crystal X-ray diffraction to 15 GPa

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ABSTRACT

High-pressure single-crystal X-ray diffraction experiments were conducted on natural cordierite crystals with composition M₄[Fe₄0.07(Fe₃0.127Si₀.873)Al₄0.062Si₁₈.960]Na₃0.026(Al₁₈.12₉) using a synchrotron X-ray source. The samples were compressed at 300 K in a diamond-anvil cell to a maximum pressure of 15.22(15) GPa with a neon pressure-transmitting medium and a gold pressure calibrant. We observed a recently described orthorhombic to phase transition, as well as a further transition to a second triclinic phase. We solved and refined both new triclinic phases in space group P1, and designate them cordierite II and III. The structures of cordierite II and III were refined at 7.52(3) and 15.22(15) GPa, respectively. The lattice parameters at these pressures are a = 15.567(3), b = 9.6235(4), c = 9.0658(6) Å, α = 89.963(5)°, β = 86.252(10)°, and γ = 90.974(8)° for cordierite II, and a = 8.5191(19), b = 8.2448(3), c = 9.1627(4) Å, α = 85.672(4)°, β = 85.986(7)°, and γ = 70.839(10)° for cordierite III. Across the phase transitions there is a significant reduction in the length of the a-axis (~2 Å per phase transition), whereas both the b- and c-axis remain largely unchanged. Cordierite II has fourfold- and fivefold-coordinated Si and Al, while cordierite III has fourfold-, fivefold-, and sixfold-coordinated Si, fourfold- and fivefold-coordinated Al, and fivefold- and sixfold-coordinated Mg. The sequence of high-pressure phases shows increasing polymerization of coordination polyhedra. These results, together with other recent studies, suggest that mixed four-, five-, and sixfold coordination states may occur more commonly in silicate structures compressed at 300 K than previously recognized.

Keywords: Cordierite, phase transition, crystallography, high pressure, single-crystal X-ray diffraction

INTRODUCTION

Cordierite is an aluminosilicate framework mineral with ideal stoichiometry of (Mg,Fe)₄Al₂Si₄O₁₂·(nCO₂, mh₂O) that crystallizes in the orthorhombic system (space group Cccm, Z = 4) at ambient conditions. It is found widely in metamorphic rocks, and plays an important role as a geothermometer, geobarometer, and monitor of fluid or melt volatile content (Currie 1971; Martignole and Sisi 1981; Carrington and Harley 1996). Due to its low thermal expansivity, it also has widespread use in applications that require high thermal-shock resistance, such as automotive parts and cookware (Hochella et al. 1979; Roy et al. 1989).

The cordierite structure consists of a network of tetrahedral (Al⁴⁺, Si⁴⁺) and octahedral (Mg⁵⁺, Fe³⁺) cation-oxygen coordination polyhedra interspersed with channels that can contain larger molecules (e.g., H₂O, CO₂) or additional cations (e.g., Na⁺). When the structure is viewed in the a-b plane, two types of layers, M-layers and T-layers, can be recognized (Figs. 1 and 2). M-layers consist of Al/Si rhombic disphenoids (tetrahedra in which all faces consist of equivalent scalene triangles such that opposite edges are equal in length) and Mg/Fe octahedra arranged in six-sided edge-sharing rings, forming a layer of interconnected rings. Within each ring, Al or Si disphenoids are edge-connected on either side to a Mg/Fe octahedron. Within a layer, a given octahedron is connected to two Si disphenoids and one Al disphenoid. T-layers consist of six-membered rings of corner-sharing Al and Si tetrahedra in a 1:2 ratio that are isolated laterally within a layer, but are cross-linked above and below by corner-sharing with the larger rings in the M-layers (Malcherek et al. 2001). The stacking of rings in the M- and T-layers results in large channels running parallel to the c-axis of the structure (Fig. 1).

At temperatures >1450 °C, cordierite adopts a high-temperature hexagonal structure that is isotypic with beryl (space group P6₃/mcc) (Schreyer and Schairer 1961; Putnis 1980a). This phase, called indialite, has Al and Si disordered over a single site (designated T₁) in the M-layers in a 2:1 ratio, and Al and Si disordered over a single site (T₂) in the T-layers in a 1:2 ratio (Meagher and Gibbs 1977). In low-temperature cordierite, the Al and Si order into distinct sites. The transformation between the hexagonal and orthorhombic phases was shown to occur by an intermediate order-modulated phase (Putnis 1980b). In orthorhombic cordierite, the T₁ site splits into two symmetrically distinct sites, the Al-occupied T₁1 site and Si-occupied T₁6, and the T₂ site splits into three symmetrically distinct sites, the Al-occupied T₂6 site and the Si-occupied T₁1 and T₁3 sites.