High-temperature crystal chemistry of hydrous Mg- and Fe-cordierites

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Abstract

Structural refinements have been completed for a Mg-rich cordierite using data recorded at 24\textdegree, 375\textdegree, 775\textdegree and 24\textdegree C (after heating to 775\textdegree) and for an Fe-rich cordierite at 24\textdegree and 375\textdegree C. The mean T-O bond lengths in both cordierites remain unchanged but the mean octahedral bonds (M-O) lengthen upon heating. The unusually low thermal expansion of the Mg-cordierite is the result of its relatively "rigid" tetrahedral framework and the anisotropic expansion of octahedra isolated from each other. This anisotropic expansion leads to a slight rotation of the six-membered rings, a concomitant collapse of the structure parallel to \textit{c}, and an expansion parallel to \(a\) and \(b\). In the Fe-cordierite, the octahedron is more flattened, resulting in \(c\) being smaller and \(a\) and \(b\) being larger than the cell dimensions of the Mg-cordierite. Upon heating Fe-cordierite, there is no evidence for a rotation of the rings, and \(a\), \(b\), and \(c\) increase as the M-O bonds expand.

X-ray \(\Delta\rho\) maps calculated for the Mg-cordierite showed approximate positions and relative amounts of channel constituents. The peak ascribed to the alkali and other atoms that centers the six-membered rings becomes elongated parallel to \(c\) upon heating through 775\textdegree C. However, the peak ascribed to the oxygen associated with H\textsubscript{2}O in the 24\textdegree and 375\textdegree C maps is absent in the 775\textdegree C maps. It reappears in maps computed from the 24\textdegree (after heating) data. In both cordierites, small amounts of hematite were produced during heating (prematurely halting data collection on the Fe-cordierite), and apparently formed by combination of octahedral and channel iron with oxygen from the channel water molecules.

A re-examination of the water orientation in the channels of the Mg-cordierite using neutron and X-ray \(\Delta\rho\) maps does not clearly show either type I (H-O-H in the (100) plane with the H-H vector parallel to \textit{c}) or type II (H-O-H in the (100) plane with the H-H vector parallel to \textit{b}) water, as previously suggested by spectroscopic studies. Instead, our \(\Delta\rho\) maps indicate that the water molecule lies in a plane tilted \(\sim 29\textdegree\) from (100) and that the H-H vector is tilted \(\sim 19\textdegree\) from \(c\).

Introduction

Cordierite, \((\text{Mg,Fe})_2\text{Al}_4\text{Si}_3\text{O}_{18} \cdot n\text{H}_2\text{O}\), has attracted the interest of mineralogists and ceramists because of its widespread formation in moderate- to high-grade metamorphic rocks, its occurrence in a variety of structural states involving different degrees of Al/Si ordering, and its unusually low thermal expansion. Ceramists have found a number of applications for Mg-cordierite as a thermal shock resistant material.