

Cordierite II: The role of CO₂ and H₂O

B.A. KOLESOV¹ AND C.A. GEIGER^{2,*}

¹Institute of Inorganic Chemistry, Lavrentiev prosp. 3, Novosibirsk 630090, Russia

²Institut für Geowissenschaften, Universität Kiel, Olshausenstrasse 40, 24098 Kiel, Germany

ABSTRACT

Polarized single-crystal Raman spectra at room temperature and 5 K and polarized infrared spectra at room temperature were obtained from four natural cordierites of different compositions in the wave number region of the CO₂ symmetric stretching vibration and the H₂O stretching vibrations. The CO₂ molecules are preferentially aligned parallel to the X axis, consistent with results from X-ray diffraction and optical studies. The CO₂ contents of six natural cordierites, previously studied by powder IR methods (Vry et al. 1990), were determined via Raman spectroscopy. A linear relationship was found between CO₂ content and the Raman intensity ratio of the normalized CO₂ stretching mode against a Si-O stretching mode. This permits a determination of the CO₂ contents in cordierite using micro-Raman measurements. The internal stretching modes between 3500 and 3800 cm⁻¹ were assigned to various types of H₂O molecules occurring in the channel cavity. Three different orientations of H₂O molecules that have no interactions with alkali cations located at 0,0,0 in the six-membered tetrahedral rings are classified in a static model as Class I H₂O molecules. The H-H vector for two of them is parallel to [001], and their molecular planes lie in the XZ and YZ crystal planes. The third type has its H-H vector directed along the X axis and its molecular plane lies in the XZ plane. Two other types of H₂O have interactions with the alkali cations located at 0,0,0. They are classified as Class II H₂O. They distinguish themselves by the number of H₂O molecules bonded to the alkali atoms. The formation of weak hydrogen bonds at low temperatures may explain the appearance of some Raman stretching modes below 200 K. The H₂O molecules of Class I-Type I/II are probably dynamically disordered about [001] hopping between orientations in the XY and XZ planes down to 5 K. Class II H₂O may also be disordered, but more measurements are required to describe its dynamic behavior.