

Polarized infrared spectrum of cordierite: orientations of water molecules and their vibrational behavior

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The ideal chemical formula of cordierite is $(\text{Mg, Fe})_2\text{Si}_5\text{Al}_4\text{O}_{18}$. Four SiO_4 tetrahedra and two opposite AlO_4 tetrahedra share corner oxygens. The stacking of these six tetrahedra along the crystallographic *c*-axis makes pipe-like cavity called a channel. The crystal system belongs to orthorhombic and space group is *Cc*cm. Natural cordierites are found in hornfels and regional metamorphic rocks. The channels of cordierite contain volatile contents such as H_2O and CO_2 . These volatiles and their behavior have been investigated since they are candidates of potential fugacity indicators. The crystal structure of cordierite is similar to that of beryl, which also has channels characterized by six SiO_4 tetrahedra. The behavior of H_2O and CO_2 in the channels of beryl are often compared with cordierite.

H_2O and CO_2 molecules are incorporated in the channels of cordierite as described above. A CO_2 molecule locates its O-C-O vector perpendicular to the *c*-axis. A water molecule generally locates its H-H vector parallel to the *c*-axis. When an extra-framework cation is trapped near a water molecule, a water molecule reorients to be its H-H vector perpendicular to the *c*-axis because of the electric attraction between a cation with oxygen of a water molecule. The former and latter forms of water molecules are called type I and type II water molecules, respectively. Extra-framework cations in the channels are incorporated to maintain the lacks of positive electrical charge balances which are caused by substitutions from ideal chemical formula. The kind of cations is generally Na^+ . The cordierite channels thus contain CO_2 and two kinds of water molecules. However, states of these volatile contents are under controversial over 40 years. Various IR bands of water are recognized depending on the three kinds of crystallographic planes of *cb*, *ca*, and *ab*-plane, since cordierite is an orthorhombic. These bands are not explained by simple fundamental vibrations of type I/II modes. Type I water molecules have interactions between channel oxygens. Type II water molecules also have interactions between extra-framework cations in addition to channel oxygens. These interactions cause the various energy variations of water vibrations. These variations of water vibrations make interpretation of water states difficult even for the cordierite which is relatively simple cyclosilicate compared to the zeolite group.

In this study, we measured polarized infrared spectra of natural cordierite samples which orient three different crystal planes, *cb*, *ca*, *ab*-plane. The spectra were measured at room temperature by changing the relative angles between *E*, the electric vector of infrared light and the crystallographic axis. The spectrum at room temperature showed the various changes of the peak ratio of type I/II water molecules with the orientation of the sample against to *E*. From these changes of spectra, we discuss the preferred orientation of type I/II water molecules in the cordierite channels. The high temperature infrared spectra were measured up to 800C. We discuss the changes of vibrations of type I/II water molecules against to temperature changes. Finally, the samples were experienced at 850C and dehydration behavior of water molecules are discussed. From the results room temperature spectra, high temperature behavior up to 800C, and the dehydration behavior at 850C for various orientated cordierite samples, we discuss the possibility of third type of water molecule, type III. These behavior of water molecules in cordierite is compared with the results of beryl which we reported previously.