

Coordinating States of Water Molecules in Beryl Channel

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Beryl is often found in pegmatite and granite pegmatite. The ideal formula is $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. The space group is P6/mcc. The crystal structure of beryl is characterized by a ring of six SiO_4 tetrahedrons. The ring stacked along the crystallographic c-axis forms a pipe-like cavity, which is called a channel. Many experimental studies showed that the channel has various extra molecules such as H_2O , CO_2 and rare gases. Cations are also incorporated in the channel to compensate the charge balance by the replacement of M^+ for Be^{2+} and M'^{2+} for Al^{3+} , where M^+ and M'^{2+} mean cations.

Two kinds of H_2O molecules have been recognized by IR and raman spectroscopy. H_2O whose H-H vector is parallel and perpendicular to c-axis is labeled as type I and type II respectively. When an H_2O is not coupled with an extra cation, it is oriented as type I. When an extra cation locates close to H_2O molecule, the oxygen of H_2O molecule is attracted by an extra cation so that H-H vector is oriented perpendicular to c-axis.

H_2O molecules of type II are accepted as being coordinated to cations. Depending on the cations or difference of coordinating state of type II, the frequency of IR absorption band must be slightly modified. However, the subtle variation of frequency due to type II is not experimentally confirmed. In natural beryl it is difficult to consider the subtle variation of frequency since water is too much incorporated in the channel.

In this study, H_2O molecule was introduced into the anhydrous beryl which was synthesized by flux fusion method. Li_2CO_3 - MoO_3 was selected as flux. Polarized IR absorption spectra were observed for the slab which was polished parallel to c-axis. Since the concentration of H_2O incorporated in the channel is limited, it enables us to consider the coordinating state of type II-cation. Two kinds of absorption bands due to type II were confirmed at 3602cm^{-1} and 3589cm^{-1} in stretching region and 1631cm^{-1} and 1619cm^{-1} in bending region. Absorption bands due to type II suggest that some cations were incorporated in the channel. We assumed that these cations are Li^+ resulting from Li_2CO_3 - MoO_3 used for flux. Li^+ must be incorporated in the channel due to the replacement of Li^+ for Be^{2+} .

Moreover, dehydration experiment was done for natural beryl to reduce the water concentration. First, step heating by manometry apparatus was done to estimate the dehydration temperature. In step heating, dehydrated amounts increased once at about 650C and increased again at about 850C. Therefore dehydration experiment was done at 850C in electronic furnace in which the duration was 2~24h. Polarized IR absorption spectra of dehydrated natural beryl were measured under $c//\mathbf{E}$, where the absorption band due to type I was not observed and the absorption band due to the vibration of type II shifted from 3592cm^{-1} to 3589cm^{-1} in stretching region and from 1625cm^{-1} to 1631cm^{-1} in bending region. Compared IR absorption spectra of dehydrated natural beryl with the result of step heating by manometry experiment, type I may dehydrate dominantly around 650C.

By analyzing the IR absorption spectra of hydrous synthetic beryl and dehydrated natural beryl, the states of type II in the channel will be discussed.