

MINERALOGICAL NOTES

Force Constant For Be–O Stretching in Behoite and in Chrysoberyl

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Abstract

An absorption band near 780 cm^{-1} in the infrared spectra of behoite [$\beta\text{-Be}(\text{OH})_2$] and of chrysoberyl [Al_2BeO_4] was assigned to the vibration of a beryllium atom moving in a tetrahedral cage of four fixed oxygen atoms. Using this simple model, a force constant of 2.4 mdyne/\AA was calculated for Be–O stretching in behoite and chrysoberyl.

Introduction

The infrared spectrum of behoite [$\beta\text{-Be}(\text{OH})_2$] was given by Ehlmann and Mitchell (1970), and the infrared spectrum of $\beta\text{-Be}(\text{OH})_2$ has been studied by Funck (1964) and by Bear, Lukaszewski, and Turnbull (1965). The $\beta\text{-Be}(\text{OH})_2$ crystal is composed of tetrahedral $\text{Be}(\text{OH})_4$ groups (Seitz, Rösler, and Schubert, 1950).

The IR spectrum of chrysoberyl [Al_2BeO_4] has been studied by Henning and Volke (1966), Povarennykh and Gevorkyan (1971), Povarennykh and Nefedov (1971), and Plyusnina (1963). Chrysoberyl contains tetrahedral BeO_4 groups and octahedral AlO_6 groups (Farrell, Fang, and Newnham, 1963).

For crystals having a small number of degrees of freedom in the unit cell, an analysis using lattice dynamics is feasible. Nusimovici (1969) has performed a lattice dynamical calculation for beryllium oxide, a crystal which contains tetrahedral BeO_4 groups. Using the Raman spectrum, he obtained a value of 2.3 mdyne/\AA for the Be–O stretching force constant.

For crystals containing the BeO_4 group but having a large number of degrees of freedom in the unit cell, the infrared spectrum is often interpreted as arising principally from the vibrations of the tetrahedral

BeO_4 group. A tetrahedral unit exhibits a non-degenerate vibration of frequency ν_1 , a doubly degenerate vibration of frequency ν_2 , and two triply degenerate vibrations at ν_3 and ν_4 (Wilson, Decius, and Cross, 1955). Generally, only ν_3 and ν_4 are infrared active, but distortions of the tetrahedral symmetry and couplings with other parts of the crystal can result in ν_1 and ν_2 appearing in the infrared and can break the degeneracy of the modes ν_2 , ν_3 , and ν_4 .

Funck (1964) has looked at ν_3 for several BeO_4 -containing molecules from the standpoint of a light central atom surrounded by heavy ligands. Using $\bar{\nu} \approx 800\text{ cm}^{-1}$ for the BeO_4 group, he obtained a metal-ligand force constant for Be–O of 1.79 mdyne/\AA .

Model for the 780 cm^{-1} Band

A simple model is proposed to account for the band near 780 cm^{-1} which occurs in the infrared spectra of several BeO_4 -containing minerals. This band is interpreted as arising from the vibration of a beryllium atom moving in a tetrahedron of fixed oxygen atoms. The frequency, ν_{Be} , of this vibration would be triply degenerate for a perfect tetrahedron, the degeneracy being broken by slight distortions of the tetrahedron.

The same procedure that would be used to evaluate the Einstein frequency of a crystal (Rice, 1967) is

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employed to express ν_{Be} in terms of the Be-O stretching force constant K . A situation is considered in which a beryllium atom experiences a displacement from equilibrium in the amount $\vec{r}_{\text{Be}} = \vec{r}_i - \vec{r}_i^*$, where \vec{r}_i is the instantaneous displacement of the beryllium atom from the i^{th} neighboring oxygen atom, and \vec{r}_i^* is the corresponding equilibrium displacement. Neglecting all but central force interactions, the potential due to the displacement \vec{r}_{Be} is given by this model as

$$V = \frac{1}{2} K \sum_{i=1}^4 (r_i - r_i^*)^2,$$

where the sum extends over the four fixed oxygen atoms.

Upon expanding $r_i = |\vec{r}_i^* + \vec{r}_{\text{Be}}|$ to first order in \vec{r}_{Be} and writing the \vec{r}_i^* in any convenient coordinate system, the simple expression

$$V = \frac{1}{2} \left(\frac{4K}{3} \right) r_{\text{Be}}^2$$

is obtained. Hence the beryllium atom behaves as a simple harmonic oscillator vibrating with a frequency

$$\nu_{\text{Be}} = \frac{1}{2\pi} \left[\frac{4K}{3} \right]^{1/2},$$

where m is the mass of a beryllium atom. This expression is similar in form to that of Funck (1964), except that ν_{Be} above shows no dependence on the mass of the outer oxygen atoms. A value for K is obtained upon assignment of an infrared band to ν_{Be} .

Using the infrared spectrum of behoite reported by Ehlmann and Mitchell (1970), a band composed of peaks at 875, 780, 750, and 720 cm^{-1} was assigned to the vibration of the Be in a tetrahedron of fixed OH groups. The average frequency, 781 cm^{-1} , was taken as $\tilde{\nu}_{\text{Be}}$. These frequencies are similar to the assignments of $\tilde{\nu}_3 = 875, 775, \text{ and } 700 \text{ cm}^{-1}$ given by Funck (1964) and close (somewhat similar) to the assignments of $\tilde{\nu}_3 = 880, 875, 825, \text{ and } 780 \text{ cm}^{-1}$ made by Bear *et al* (1965).

A band in the infrared spectrum of chrysoberyl with peaks at 750, 775, and 820 cm^{-1} was tentatively assigned to $\tilde{\nu}_3$ by Henning and Volke (1966). The average of these peaks, 782 cm^{-1} , is close to the assignment of 780 cm^{-1} made for $\tilde{\nu}_3$ by Povarennykh and Nefedov (1971), and is not inconsistent with the

assignment of $\tilde{\nu}_3 = 1000, 860 \text{ and } 780 \text{ cm}^{-1}$ given by Povarennykh and Gevorkyan (1971). A quite different assignment was given by Plyusnina (1963) who tentatively assigned to $\tilde{\nu}_3$ a band having peaks ranging from 963 to 1161 cm^{-1} .

Using the frequency 780 cm^{-1} for $\tilde{\nu}_{\text{Be}}$ in both behoite and chrysoberyl, a Be-O stretching constant of $K = 2.4 \text{ mdyne/\AA}$ is obtained, in good agreement with the Be-O stretching constant of 2.3 mdyne/\AA obtained by Nusimovici (1969) for beryllium oxide.

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