FTIR spectroscopy of D$_2$O and HDO molecules in the c-axis channels of synthetic beryl

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ABSTRACT

This paper presents the results of Fourier transform infrared (FTIR) spectroscopy of a synthetic beryl, containing D$_2$O molecules in its c-axis channels, which we synthesized under hydrothermal conditions at 600 °C and 1.5 kbar. The frequencies of absorbance bands in the range of the stretching vibrations and their overtones and combination modes for D$_2$O and HDO molecules have been assigned for the first time. On the basis of our assignments, the absorbance bands observed for the natural beryl in the range of the OD stretching vibrations have been explained.

Keywords: Beryl; emerald; FTIR spectroscopy; H$_2$O, D$_2$O, and HDO molecules

INTRODUCTION

The nature of water entering into the structure of beryl has attracted the attention of researchers for more than half a century (Wood and Nassau 1967 and references therein). Beryl, with ideal formula Al$_2$Be$_3$(Si$_6$O$_{18}$), crystallizes in a hexagonal structure with space group $P6/mmc$ ($D_{6h}^1$). Its honeycomb structure consists of six-membered rings (Si$_6$O$_{18}$)$^{12–}$ linked together by tetrahedrally coordinated Be ions and octahedrally coordinated Al ions. These six-membered rings are stacked one above the other, forming channels parallel to the c-axis (hereafter c-channels). These channels are formed by cavities approximately 5.1 Å in diameter, which are separated by “bottlenecks” of 2.8 Å in diameter. There are two types of structural positions in c-channels: position 2a, with 62 ($D_3^h$) symmetry in the center of cavity surrounded by 24 oxygen atoms; and position 2b, with 6/m ($C_{6v}$) symmetry in the center of a six-membered ring. The distance between two neighboring cavities is about 4.6 Å along the c-channel. The width of these cavities is sufficient to incorporate single molecules of H$_2$O, CO$_2$, N$_2$, and HCl, as well as ions of NH$_4^+$ and inert gases of He and Ar (Damon and Kulp 1958; Mashkovtsev and Solntsev 2002; Mashkovtsev and Smirnov 2004; Mashkovtsev and Thomas 2005; Wahler 1956; Wood and Nassau 1967; Zimmerman et al. 1997).

H$_2$O molecules in the c-channels have been mainly classified as type I or type II water with their twofold axis perpendicular or parallel to the crystal c-axis, respectively (Wood and Nassau 1967). Normal (unsubstituted or weakly substituted) beryl shows an almost exclusive presence of type I water, whereas type II water becomes dominant when cationic substitution, in fourfold or sixfold coordination, and the content of Li and Na increases (Aines and Rossman 1984; Aurisicchio et al. 1994; Charoy et al. 1996; Łodziński et al. 2005; Della Ventura et al. 2007). It has been found that an H$_2$O molecule adjacent to an alkali ion may change its orientation from perpendicular to parallel, due to the effect of the electric field of the charged alkali ion. However, there are currently no clear definitions for the frequencies of type II water molecule stretching bands and type I molecule symmetric band $n_s$ as summarized in the tables compiled by Charoy et al. (1996) and Makreski and Jovanvski (2009). Fukuda and Shinoda (2008) distinguished between type II water molecules coordinated by single or double sodium ions based on $n_1$ and $n_2$ frequency shifts. The findings of Fukuda and Shinoda (2008) were supported by the study of Della Ventura et al. (2015) who added the data on $n_3$ frequency shift. In flux-grown emerald Bellatreccia et al. (2008) studied exclusively type II water molecules that are probably associated with Li impurities.

There are only a few publications (De Donato et al. 2004; Manier-Blaginéa et al. 1989; Zwaan et al. 2012) that have studied D$_2$O molecules in the c-channels of beryl by infrared (IR) spectroscopy. The two stretching modes at 2744 and 2630 cm$^{-1}$ were ascribed to the type I D$_2$O molecule based on the experiments with natural beryl powder treated with DCl solutions (Manier-Blaginéa et al. 1989). The IR spectra of D$_2$O and HDO molecules in beryl single crystals with the natural isotopic abundance were observed by De Donato et al. (2004) and Zwaan et al. (2012), but no complete assignment of the OD bands in the stretching-vibration region was done.

Zhukova et al. (2014) and Gorshunov et al. (2013), who explored the dynamics of H$_2$O molecules confined in the structural channels of beryl using terahertz-infrared spectroscopy, proposed a model, explaining the fine structure of the observed infrared absorption bands. To test the validity of this model, we synthesized a unique type of beryl single crystals, containing D$_2$O in place of H$_2$O molecules. We aim here to assign the infrared absorbance bands of D$_2$O and HDO molecules in the c-channels of beryl using FTIR spectroscopy.

EXPERIMENTAL METHODS

H$_2$O, D$_2$O, and HDO bearing beryls were synthesized by the hydrothermal method of Thomas and Klyakhin (1987). Three crystals, no. 3855, no. 3871, and no. 3875, with dimensions about 1 × 2 × 3 cm were grown on the seed plates from oxides at 600 °C and 1.5 kbar in a hermetically sealed gold vessel. All reagents...