FTIR SPECTROSCOPY OF OH DEFECTS IN NOMINALLY ANHYDROUS MINERALS (KYANITE, ANDALUSITE, OLIVINE AND TRIPHYLLITE)

by

Arkadiusz Wieczorek

Doctoral Thesis Faculty of Natural Sciences and Mathematics, University of Vienna

> Institute of Mineralogy and Cristallography Vienna, June 2005

Analyses of kyanite samples from 10 different localities presented in this work show, that only colourless parts of samples contain visible OH absorption bands, with exception of kyanite from Roberts Victor mine. On the basis of IR absorption spectra, the samples can be divided into three types: 1) Roberts Victor mine, 2) Pamir and Kilimandjaro, and 3) Pizzo Forno. To the third type kynite from Dora Maira can be added, however, the IR spectra of this sample show many exceptional features. The differences of IR spectra between not heated and dehydrated samples suggest that only bands at 3260, 3275, 3295, 3410 and 3440 cm⁻¹ represents OH defects in the kyanite structure, whereas bands in the 3450-3650 and 3290-3350 cm⁻¹ regions are due to solid inclusions, like layer silicates. Based on the pleochroic behaviour of absorption bands, an OH incorporation model is proposed, with O1, O2, O3, O6, O8 and O10 oxygen atoms of the kyanite structure partially replaced by OH defects. This model extends the OH incorporation model proposed by BERAN (1971), in which only O6 and O2 oxygen atoms were partially replaced by OH defects. The water contents in kyanite obtained in this study vary between 5 and 21 wt ppm H₂O.

Investigations of andalsuite samples show more detailed IR spectra than previously published, especially appearance of the double-band with maxima at 3527 and 3517 cm⁻¹ was not observed before. Nevertheless, the obtained results confirm previous observations and the OH observed before. Nevertheless, the obtained results confirm previous observations and the OH incorporation model proposed by BERAN & ZEMANN (1969), in which the O2 oxygen atoms are partially replaced by OH defects. In andalusite the water content values are around 130 wt ppm H₂O.

The olivine samples from Norway analysed in this work have similar IR spectra as previously investigated forsterites (MILLER et al., 1987; LIBOWITZKY & BERAN, 1995). The observed pleochroic behaviour of absorption bands is in agreement with the OH defects incorporation model proposed by BERAN & PUTNIS (1983), in which the O1-H group is pointing toward a vacant Si site.

In comparison, triphylite (LiFePO4), which is isostructural with olivine, has all its OH defects oriented along the crystallographic c axis. An OH incorporation model with an O3-H group pointing toward another O3 atom is proposed, together with the presence of Fe vacancies. In both minerals the water content is very similar. i.e. ca. 6 wt ppm, H_2O for olivine and 4 wt ppm H_2O for triphylite.

The investigation and results presented in this work are part of the European Union research program "Human Potential-Research Training Networks", and the project "Hydrogen Speciation in Upper Mantle Minerals" (HYDROSPEC).

Literature

- BERAN, A. (1971): Messung des Ultrarot-Pleochroismus von Mineralen. XII. Der Pleochroismus der OH-Streckfrequenz in Disthen. - Tschermaks Mineralogische und Petrographische Mitteilungen, 16, 129-135.
- BERAN, A. & ZEMANN, J. (1969): Messung des Ultrarot-Pleochroismus von Mineralen. VIII. Der Pleochroismus der OH-Streckfrequenz in Andalusit. - Tschermaks Mineralogische und Petrographische Mitteilungen, 13, 285-292.
- BERAN, A. & PUTNIS, A. (1983): A model of the OH positions in olivine, derived from infrared-spectroscopic investigations. - Physics and Chemistry of Minerals, 9, 57-60.
- LIBOWITZKY, E. & BERAN, A. (1995): OH defects in Forsterite. Physics and Chemistry of Minerals, 22, 387-392.
- MILLER, G. H., ROSSMAN, G. R. & HARLOW, G. E. (1987): The natural occurrence of hydroxide in olivine. - Physics and Chemistry of Minerals, 14, 461-472.