Integral molar absorptivities of OH in muscovite at 20 to 650 °C by in-situ high-temperature IR microspectroscopy

KAZUYO TOKIWA and SATORU NAKASHIMA*

Department of Earth and Space Science, Graduate School of Science, Osaka University, Machikaneyama-cho 1-1, Toyonaka, Osaka, 560-0043, Japan

ABSTRACT

The change with temperature of IR absorption bands in OH in muscovite was studied using unpolarized in-situ high-temperature infrared microspectroscopy. The molar absorption coefficient ε at 3628 cm\(^{-1}\) for OH in muscovite at room temperature (20 °C) has been determined to be 127 ± 6 L/mol·cm. Using the orientation factor γ = 0.47 for the angle between OH vector and c* axis (75 ± 5°), the true molar absorption coefficient ε at 3628 cm\(^{-1}\) is determined to be 270 ± 10 L/mol·cm at 20 °C. Integral molar absorptivities are also determined from 20 to 650 °C showing no weight loss. The value decreases from 7060 ± 190 L/mol·cm\(^2\) at 20 °C to 5190 ± 270 L/mol·cm\(^2\) at 650 °C (26% decrease). OH orientation of muscovite sample measured by polarized IR microspectroscopy at 20 °C showed that the angle between the projection of OH vector to (001) plane (the OH′ vector) and b axis is 30.5° at 20 °C and did not change greatly at higher temperatures up to 650 °C. The tilting of OH dipoles toward the c* axis from 75° to about 43° while keeping the same angles along b axis would explain the observed decrease in integral molar absorptivities at higher temperatures, but further studies are needed to clarify the OH behavior at high temperatures.

Keywords: Muscovite, OH, in-situ high-temperature IR microspectroscopy, integral molar absorptivity, OH orientation

INTRODUCTION

Water in minerals and melts is an essential factor for the dynamics of Earth and planetary materials (Aines and Rossman 1984). The concentrations of OH and H\(_2\)O in hydrous minerals and melts are often determined by IR spectroscopy at room temperature from intensities of the absorption bands of water species using the molar absorptivities [e.g., for silicate melts, Stolper (1982); Dobson et al. (1989); Ihinger et al. (1994); Dixon et al. (1995); Yamashita et al. (1999); Ohlhorst et al. (2001); Okumura et al. (2003)].

Since molar absorptivity data for OH in minerals are limited for certain minerals, several empirical relationships have been proposed for evaluating linear and integral molar absorptivities for OH in minerals where experimental data are missing (Paterson 1982; Libowitzky and Rossman 1997; Libowitzky and Beran 2004). However, direct determination of linear and integral molar absorptivities for OH in various minerals is preferable.

High-temperature IR studies have also been conducted using a heating stage, diamond cell, and sapphire cell under IR microscopes (e.g., Keppler and Bagdassarov 1993; Nowak and Behrens 1995, 2001; Shen and Keppler 1995; Withers et al. 1999). The in-situ IR technique directly measures the concentrations of OH and H\(_2\)O at high temperatures, but often lacks calibration data for high-temperature molar absorptivity. Only a few studies (Yamagishi et al. 1997; Sowerby and Keppler 1999; Withers et al. 1999; Nowak and Behrens 2001; Okumura and Nakashima 2005) have evaluated high-temperature molar absorptivities of OH and H\(_2\)O in minerals and glasses. However, more data on representative hydrous minerals are needed.

Sample characterization

The starting material used in this study is muscovite-2M1 from Ishikawa, Fukushima, Japan. The chemical composition of the sample was analyzed with a JEOL-JXA-8800M electron microprobe using a defocused beam (10 \(\mu\)m in diameter), 15 kV accelerating voltage, and 12 nA beam current. The analytical results are listed in Table 1. Minor elements such as F and Li were below the detection limit of the EMPA analysis and have not been determined.

The water content of the powdered sample was determined by thermal analysis. Thermogravimetry (TG) was carried out using a SII TG/DTA 6000 instrument from 23 to 1100 °C with a heating rate of 10 °C/min (Fig. 1). The TG curve in Figure 1 shows a weight loss of about 2% up to about 200 °C, which may be attributed to adsorbed water (Guggenheim et al. 1987). The weight loss in the range from 200 to 950 °C is 4.46 ± 0.24 wt%. Thus, the water content of muscovite was determined to be 4.46