Feasibility of determining the quantitative OH content of garnets with Raman spectroscopy

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ABSTRACT

Two suites of garnets were examined by infrared absorption spectroscopy and depolarized Raman spectroscopy to determine if the Raman signal could be used as a quantitative measurement of OH content. To avoid the problems of determining the absolute Raman signal intensity, the integrated intensity of the OH bands was ratioed to the integrated intensity of silicate Si-O stretching bands and used as a proxy for the OH intensity. These were compared to the OH contents, expressed as wt% H$_2$O, independently determined from infrared absorption. A somewhat useful trend developed between OH contents determined by Raman and IR for some grossular garnets with H$_2$O contents less than 0.5%. Many colorless to near-colorless grossular garnets do not provide a useful Raman signal due to fluorescence, although other samples with H$_2$O contents between 0.5 and 1.3 wt% and are strongly colored, fall far below the trend of the samples with lower H$_2$O-contents. Spessartine-almandine garnets from the Rutherford no. 2 pegmatite all respond to the Raman experiment, but produce a confusing trend when compared to H$_2$O. Coincidentally, a relatively smooth but decreasing trend was observed when the spessartine Raman OH intensity ratio was compared to the iron content. These observations suggest that Raman measurements by this method are not suitable, in general, for the determination of OH in garnets.

INTRODUCTION

Hydroxide ions are a minor component of many silicate minerals that are usually formulated as anhydrous. In garnets, the concentration of OH can range from trace levels to that of a major component. Hydroxyl in garnet has been extensively studied with infrared transmission spectroscopy, and analytical calibrations have been established through integrated absorbance and peak heights for the spessartine-almandine series (Rossman et al. 1988), for grossular (Rossman and Aines 1991), and for pyrope (Bell et al. 1995). Although infrared methods are comparatively easy to conduct, they do require that the sample be prepared as a doubly polished slab of thickness appropriate for the amount of OH in the sample. Because Raman spectroscopy is a relatively fast and easy way to collect data with minimal sample preparation, we wanted to evaluate the utility of this method to acquire quantitative OH concentrations for some members of the garnet family. Available for this study were the suite of grossular samples used by Rossman and Aines (1991) in their study of OH in grossular, and the suite of spessartine-almandine garnets from the Rutherford no. 2 pegmatite used by Arredondo et al. (2001). Analyses by Raman spectra have proven useful for determining water contents of melt inclusions in granite with contents ranging from 0–20 wt% (Thomas 2000). The goal of this project was to determine if Raman spectra could provide the same quantitative measure of OH contents that can now be obtained by infrared transmission spectra.

EXPERIMENTAL METHODS

Sample description

Forty-one grossular and ten spessartine-almandine garnets with OH concentrations previously determined by infrared spectroscopy were analyzed for this study. The grossular garnets range from colorless to green to brown-orange. Their OH concentrations range from colorless to green to brown-orange. Their OH concentrations were determined by Arredondo et al. (2001), range from 0.02 to 0.16 wt% H$_2$O. With certain samples having approximately 9 to 12 OH per formula unit. The spessartine-almandine garnets range from deep red (Sp$_{45}$) to pale orange (Sp$_{91}$) in color. Their OH concentrations, determined by Arredondo et al. (2001), range from 0.02 to 0.16 wt% H$_2$O. Full descriptions of the samples are presented in Rossman and Aines (1991) and Arredondo et al. (2001).

Infrared OH analysis

When needed, re-analyses of samples used in prior studies were conducted on a Nicolet Magna 860 FTIR operating at 4 cm$^{-1}$ resolution. Each sample was doubly polished and the clearest portion was mounted over a steel pinhole aperture ranging from 100 to 400 micrometers in diameter. Hydroxyl contents were determined from the integrated area of the OH stretching bands as detailed in Rossman and Aines (1991), and Arredondo et al. (2001).