INTRODUCTION

There is great current interest in understanding interactions, especially at the atomistic or molecular level, between \( \text{H}_2\text{O} \) and its components (e.g., \( \text{H}^+, \text{OH}^–, \text{H}_2, \text{O}_2 \)) and Earth materials. Hydrothermal ore deposition, chemical weathering of various materials, and many metamorphic reactions are important examples of the types of processes that are largely controlled by the nature of \( \text{H}_2\text{O} \)-rich fluids and their interplay with solid phases. From a mineralogical or crystal-chemical standpoint, much effort has been made over the past approximately 30 years in investigating how \( \text{OH}^– \) can be incorporated into nominally anhydrous (rock-forming) minerals, or NAMS as they are now often referred to, following early studies by Martin and Donnay (1972) and Wilkins and Sabine (1973), for example. Here, questions such as the bulk water content of the mantle, and what phases can incorporate \( \text{OH}^– \), and in what concentrations, come immediately to mind. Thus, a good deal of research has focused on pyroxene, olivine, and garnet (e.g., Bell and Rossman 1992). All of these silicates are capable of incorporating small concentrations of \( \text{OH}^– \) at mantle conditions. However, in spite of the amount of research that has been done, it is still poorly understood where the \( \text{OH}^– \) is located in their structures or through what substitution mechanism(s) it has been incorporated. In this regard, the hydrogarnet substitution (i.e., \( \text{O}_4\text{H}_4 \leftrightarrow \text{SiO}_4 \)) has received special attention, because it is a verified mechanism for incorporating of \( \text{OH}^– \) in garnet (Cohen-Addad et al. 1967; Foreman 1968; Lager et al. 1987; Ambruster and Lager 1989) and possibly in other silicates as well. Indeed, at relatively low geologic temperatures there is complete solid solution between grossular, \( \text{Ca}_3\text{Al}_2(\text{SiO}_4)_3 \), and hydrogrossular, \( \text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3 \), as was shown a number of years ago by Flint et al. (1941). It can be stated that this substitution offers a simple starting point for investigating and understanding the crystal-chemical nature of \( \text{OH}^– \) in garnet.

The primary experimental tool that is used in this type of study has been single-crystal IR spectroscopy. Raman spectroscopy has also been used but to a lesser degree. However, because the IR spectra of natural garnets are often quite complicated, inasmuch as they show a plethora of different spectra (see Rossman and Aines 1991 for grossular-hydrogrossular garnets as an example), work on compositionally simple garnets (pyrope, almandine, grossular, and nearly end-member compositions) that have been synthesized hydrothermally under controlled conditions (Geiger