The hydrous component in andradite garnet

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ABSTRACT

Twenty-two andradite samples from a variety of geological environments and two synthetic hydroandradite samples were studied by Fourier transform IR spectroscopy. Their spectra show that H enters andradite in the form of OH. Amounts up to 6 wt% H₂O occur in these samples; those from low-temperature formations contain the most OH⁻⁻. Some features in the absorption spectra indicate the hydrogarnet substitution (SiO₄)⁴⁻⁻↔(O₄H₄)⁴⁻⁻ whereas others indicate additional types of OH⁻⁻ incorporation. The complexity of the increases with increasing complexity of the garnet composition.

INTRODUCTION

Systematic studies have shown that hydroxide is a common minor component of grossular and pyrope-almandine-spsesandite garnets (Aines and Rossman 1985; Rossman and Aines 1991). Comparable surveys of andradite garnet have not been previously presented. Several reports indicate that appreciable amounts of OH⁻⁻ can be incorporated in both natural and synthetic andradite-rich garnet (Flint et al. 1941; Peters 1965; Gustafson 1974; Suwa et al. 1976; Onuki et al. 1982; Huckenholz and Fehr 1982; Marcke de Lummen 1986; Kobayashi and Shoji 1987; Kühberger et al. 1989; Wise and Moller 1990; Armbruster and Geiger 1993; Armbruster 1995). Furthermore, elevated OH⁻⁻ contents have been reported in other Fe³⁺-rich garnets such as melanite (Lager et al. 1989) and schorlomite (Locock et al. 1995), which suggests that H incorporation in Ca-Fe²⁺ garnet may be a general phenomenon. Solid-solution relationships between andradite, Ca₃Fe₂(SiO₄)₃, and hydroandradite, Ca₃Fe₂(OH)₄, are now established experimentally, and the amount of the hydroandradite component in andradite may be used as geothermometer (Huckenholz and Fehr 1982).

Only a few of these studies provide direct evidence of structural OH⁻⁻ in andradites by spectroscopic or diffraction methods. Kobayashi and Shoji (1987) report IR spectra of some synthetic andradite-hydroandradite solid solutions. Locock et al. (1995) report an absorption band due to OH⁻⁻ at 3564 cm⁻¹ in the IR spectrum of the Ice River schorlomite with 0.036 wt% H₂O. In a crystallographic study, Lager et al. (1989) were unable to locate the H in an andradite (melanite variety) with up to 14% of the Si sites empty. In such H-rich garnets, OH⁻⁻ most probably occupies tetrahedral sites wherein charge balance is achieved by the well-known hydrogarnet substitution (O₄H₄)⁴⁻⁻↔(SiO₄)⁴⁻⁻. This observation has been confirmed by XRD of a hydrous andradite with a Si deficiency of about 50%, and a high OH content (Armbruster 1995). The structure of this particular sample with space group Ia3d is composed of disordered microdomains containing (SiO₄) and (O₄H₄) tetrahedral units.

The aim of the present investigation was to perform a Fourier transform infrared (FTIR) study on different samples of andradite (including Ti-rich melanite) from various geological environments, i.e., different pressures and temperatures of formation, to determine (1) if various types of structural incorporation of OH⁻⁻ occurs in andradite as in other natural garnets or if there is only the hydrogarnet substitution; (2) the amount of OH that is incorporated in natural andradites; (3) if a correlation exists between the chemical composition and the complexity of the spectra; and (4) the pressure and temperature dependence of OH⁻⁻ incorporation. Finally, (5) we compare spectroscopic properties of OH⁻⁻ in natural garnets to those in synthetic hydroandradite.

EXPERIMENTAL METHODS

Samples were obtained mainly from museums. Details of samples, localities, and geological environments are presented in Table 1. The IR spectra of the natural crystals were recorded from doubly polished single crystals with almost parallel surfaces. The thicknesses of the platelets were between 11.5 and 1185 μm. Measurements were made on clear and inclusion-free as well as crack-free areas of the crystals. In those crystals where color zonation was present, spectra were taken from a selected number of relatively homogeneous parts of the crystal. IR spectra were measured from 114 μm × 114 μm areas using a Nicolet 60SX-FTIR spectrometer equipped with the NicPlan IR microscope and an HgCdTe detector (Rossman and Aines 1991). A 15x reflecting objective and a 10x condenser were used for the measurements. A resolution of 2 cm⁻¹