Computer simulation of the infrared and Raman activity of pyrope garnet, and assignment of calculated modes to specific atomic motions

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ABSTRACT

The lattice dynamics computer code PARAPOCS was successfully used to calculate the 240 vibrational frequencies of pyrope garnet, Mg$_3$Al$_2$Si$_3$O$_{12}$, at ambient conditions. The atomic displacement vectors (eigenvectors) for each frequency were also calculated and their symmetry relations analyzed with the aid of factor group analysis (FGA), to determine the symmetry species of each vibrational mode. Comparison with the experimental IR and Raman data shows excellent agreement, but no LO-TO reversals were identified. Calculation of the frequency shifts due to the isotopic substitution of $^{26}$Mg and $^{30}$Si, together with a more detailed analysis of the calculated eigenvectors, enabled identification of the dominant site or cation motion contributing to each vibrational mode. Previous assignments of the high-frequency vibrations to pure SiO$_4$ internal modes and the lower-frequency vibrations to mixed cation modes are supported. We conclude that the specific number of site/atom motions predicted by site group analysis (SGA) is not adhered to due to substantial mode mixing, and that FGA and SGA, in which the SiO$_4$ tetrahedra are treated as isolated units, are only applicable at high frequencies. The agreement observed between the calculated and experimental data leads us to conclude that the method of computer modeling used and the interatomic potentials employed in the simulations provide a good description of the lattice dynamical behavior of pyrope garnet.

INTRODUCTION

Garnets are important metamorphic minerals observed at the Earth’s surface and are fundamental constituents of the Earth’s upper mantle and transition zone. According to most petrological models, the garnet solid-solution series forms approximately 15% of the upper mantle and this volume fraction increases in the transition zone due to the dissolution of up to 80% pyroxene into the garnet structure (Ringwood 1967, 1970; Akaogi and Akimoto 1977; Gasparik 1989). Below 300 km, pyrope, Mg$_3$Al$_2$Si$_3$O$_{12}$, forms an important solid-solution with majorite, Mg$_4$Si$_4$O$_{12}$ (Ringwood and Major 1971; Akaogi and Akimoto 1977; McMillan et al. 1989; Gasparik 1989, 1990; Sinogeiken et al. 1997; Heinemann et al. 1997). Hence, it is important to have an accurate determination of the vibrational properties of pyrope as these govern its macroscopic behavior and therefore influence the characteristics of the phases along the binary join.

Powder-dispersion IR spectra of pyrope-rich garnets (Adler et al. 1950; Launer 1952; Wickersheim et al. 1960; Tarte 1965; Moore et al. 1971; Cahay et al. 1981; Geiger et al. 1989, 1992; and Bosenick et al. 1995) commonly yield fewer than the expected 17 modes. Measurements of this type encounter significant scattering and give peak positions that lie between the LO and TO frequencies according to the powder density and particle thickness used. In contrast, the single-crystal reflectance data of Hofmeister and Chopelas (1991) and Hofmeister et al. (1996) give a quantitative and complete set of IR-active bands for pyrope and demonstrate that accidental degeneracies occur for two of the IR modes.

Raman spectroscopic studies of pyrope-rich garnets are less common. Griffith (1969) presented six Raman-active bands in the range 300–1000 cm$^{-1}$, and the subsequent Raman studies were still limited when Mernagh and Liu (1990) reported only 7 out of the expected 25 Raman-active modes in the range 100–1200 cm$^{-1}$. Hofmeister and Chopelas (1991) made polarized single-crystal Raman measurements of pyrope and reported the first complete set of 25 Raman-active bands. Later studies by authors such as Kolesov and Geiger (1998) and Gillet et al. (1992) have presented a maximum of 17 and 19 bands, respectively, in the same range.

The number of IR and Raman spectroscopic studies of garnets with various compositions reporting incomplete sets of modes illustrates the necessity for single-crystal and polarized studies of solid-solutions, and the care required to distinguish between weak modes and artifacts. Computer simulations can augment these difficult experiments through the prediction of vibrational frequencies and their IR and Raman-activity. In this paper, we present the first complete set of calculated Raman-active and IR-active vibrational modes (including LO-TO splittings) for pyrope garnet. We also assign the modes to dominant site...