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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, $Mg_3Al_2Si_3O_{12}$, 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.