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The IR vibrational properties of six members of the garnet family: A quantum mechanical ab initio study

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Abstract

The IR vibrational properties and the corresponding reflectance spectra of the six most common members of the garnet family (pyrope $Mg_3Al_2Si_3O_{12}$, almandine $Fe_3Al_2Si_3O_{12}$, spessartine $Mn_3Al_2Si_3O_{12}$, grossular $Ca_3Al_2Si_3O_{12}$, uvarovite $Ca_3Cr_2Si_3O_{12}$, and andradite $Ca_3Fe_2Si_3O_{12}$) were simulated at the ab initio level with the CRYSTAL09 code by using a large all-electron Gaussian-type basis set and the B3LYP hybrid functional. The 17 IR active F_{1u} transverse optical (TO) and longitudinal optical (LO) frequencies, the oscillator strengths, the high frequency and static dielectric constants, and the reflectance spectrum were computed. The agreement with experiments for the TO and LO peaks is always excellent, the mean absolute difference for the whole set of data (overall 178 peaks) being 5 cm^{-1}. Oscillator strengths, calculated from the mass-weighted effective Born charges, are found in semi-quantitative agreement with the experimental data. The reflectance spectra, simulated through the classical dispersion relation, reproduce the experimental curves extremely well. The availability of the full set of simulated frequencies and intensities, obtained by using uniform computational tools (computer code, variational basis sets, density functional), permits the establishment of correlations between IR wavenumbers and structural features suggested, but only partially documented, in the past.

Keywords: Garnet, IR frequencies, IR intensities, reflectance spectrum, ab initio calculations, all-electron gaussian basis sets, B3LYP functional, CRYSTAL code