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The infrared vibrational spectrum of andradite-grossular solid solutions: A quantum mechanical simulation

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Abstract

Infrared spectroscopy is a powerful technique for the characterization of minerals, permitting insights into their structural and thermodynamic properties. The intrinsic complexity of mineral solid solutions makes the interpretation of their spectroscopic data a challenging task.

In this work, the IR vibrational spectra of andradite-grossular ($Ca_3Fe_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$) solid solutions 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. All the 23 symmetry-independent configurations resulting from the substitution of 1 to 8 Fe atoms with Al atoms in the 16*a* octahedral site of the andradite primitive cell were considered. The IR active transverse optical frequencies and their intensities were computed. Graphical representation of the spectra, animation of the modes and isotopic substitution of the cations were used as additional interpretation tools. The dominant high-frequency modes, corresponding to Si-O stretching motions, show a simple linear behavior of both frequencies and intensities with respect to the binary composition; this trend is related to the linear behavior of the mean lattice parameter. Also the frequencies of the low-energy bands show, roughly speaking, a linear dependence on composition; however, the behavior of the dominant intensities is more complicated and strongly connected to the Al and Fe atomic fraction. When considering different possible structures at fixed composition, some spectral features display a dependence upon short-range Y cation ordering. Overall, we show how ab initio calculations permit to analyze complex systems such as solid solutions, establishing relations among structure and properties and providing critical and robust interpretations to the experimental findings.

Keywords: Garnets, andradite, grossular, solid solutions, IR frequencies, IR intensities, ab initio calculations, all-electron Gaussian basis sets, B3LYP, CRYSTAL code