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 MgSi3O12, almandine Fe2Al3Si3O12, grossular Ca3Al2Si3O12, uvarovite Ca3Cr2Si3O12, and andradite Ca3Fe2Si3O12) 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 F1u, 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 excellent agreement with the experimental data. The reflectance spectra, simulated through 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

INTRODUCTION

Garnets, X3Y2Si3O12, are important rock-forming silicates, as major constituents of the Earth’s upper mantle and as relevant phases of high-pressure metamorphic rocks in the Earth’s crust (Deer et al. 1992). From a technological point of view, they are largely used for various industrial applications, for example filtration media and abrasives, thanks to their recyclability and high hardness (Olson 2001). Pyrope MgSi3O12 (Prp), almandine Fe2Al3Si3O12 (Adr), grossular Ca3Al2Si3O12 (Grs), uvarovite Ca3Cr2Si3O12 (Uv), and andradite Ca3Fe2Si3O12 (Adr) are the most common members of the family.

Garnets, despite their relatively complex structure, represent excellent reference systems for the study of the vibrational properties of silicates. Their large unit cell (80 atoms) is characterized by high symmetry (space group Pmmm). The building blocks are SiO4 tetrahedra that share corners with YO4 octahedra; X2⁺ cations are in dodecahedral coordination. Because of the high symmetry, garnets present a relatively simple vibrational spectrum (17 IR and 25 Raman active modes). The vibrational properties have been extensively investigated with various experimental techniques (Hofmeister and Chopelas 1991a; Hofmeister et al. 1996; McAlloon and Hofmeister 1995; Kolesov and Geiger 1998, 2000; Chopelas 2005). In particular, Hofmeister and others (Hofmeister and Chopelas 1991a; Hofmeister et al. 1996; McAlloon and Hofmeister 1995) conducted a detailed infrared (IR) reflectance study on single-crystal samples of five end-members of the garnet family. This nearly complete and homogeneous set of data represents an ideal reference for a computational investigation.

In previous papers (Pascale et al. 2005a, 2005b; Zicovich-Wilson et al. 2008; Valenzano et al. 2009; Ferrari et al. 2009; Valenzano et al. 2010; Dovesi et al. 2009b), transverse optical (TO) and longitudinal optical (LO) IR-active frequencies, together with TO-LO splitting values, were calculated and compared with experimental data for each of the six garnets. The agreement between simulated and observed values was found to be excellent, as indicated by the mean absolute difference |Δν| (<10 cm⁻¹).

Recently new tools have been implemented in the CRYSTAL code that permit one to evaluate the oscillator strengths (Maschio et al. 2011) and the dielectric tensor (Ferrero et al. 2008a, 2008b). A comparison with experiments can then be extended to these two new features, and to the reflectance spectrum R(ν) that is now generated automatically by the CRYSTAL code (preliminary results have been published for Alm by Ferrari et al. 2009). R(ν) is the primary experimental information from which the position and intensity of the peaks are obtained, such that the accessibility of R(ν) permits a more direct comparison with experiments.

The main purpose of the present paper is to present and discuss these new CRYSTAL code features. A second motivating factor is to establish correlations between spectral features,