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Hydrogrossular, $Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$: An ab initio investigation of its structural and energetic properties

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Abstract

Structural and energetic properties of the grossular-katoite solid solution are studied with a full ab initio quantum chemical approach. An all-electron basis set and the hybrid B3LYP functional are used. Calculations are performed within the primitive cell of cubic garnets. The hydrogarnet substitution, $SiO_4 \leftrightarrow H_4O_4$, yields 136 symmetry-independent configurations ranging from triclinic to cubic symmetry. All of them have been structurally optimized, the relaxed geometries being characterized by pseudo-cubic conventional cells. At the present level of approximation, the most stable configurations constitute by far the largest contributions to the system properties. Considering only the most stable configurations, average geometrical features of the actual solid solution are closely approximated. The excess volume displays a highly non-ideal behavior that is favorably compared with carefully analyzed and selected experimental data. The excess enthalpy deviates from the regular model; it draws an asymmetric function of composition with two minima that can be associated to structures or compositions observed in nature. Geometrical variations and distribution of the tetrahedra are analyzed. Calculations provide independent support to the use of a split-atom model for experimental refinements on these compounds. The asymmetry of the enthalpy of mixing can be associated with two distinct distribution patterns of the tetrahedra. Hydrogen interactions also contribute to the asymmetry of the excess enthalpy, as it turns out by comparison between compositions close to fully hydrated katoite and those close to grossular. Hydrogen interactions in Si-free katoite are found to be weak as suggested by dramatic changes in the H environment associated with the introduction of SiO_4 tetrahedra.

Keywords: Hydrogarnet, hydrogrossular, grossular, hibschite, katoite, solid solution, ab initio, Crystal code