Hydrogrossular, \( \text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{H}_4\text{O}_4)_x \): 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, \( \text{SiO}_4 \leftrightarrow \text{H}_4\text{O}_4 \), 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

**Introduction**

Silicate garnets are nominally anhydrous minerals (NAMs) with stoichiometry \( X_3Y_2(\text{SiO}_4)_3 \), which, nonetheless, have been found to commonly contain hydrous components. Garnets characterized by a hydrous component fall under the general heading of hydrogarnets. They are crystalline solid solutions of general formula \( X_3Y_2(\text{SiO}_4)_{3-x} (\text{H}_4\text{O}_4)_x \), whose composition varies through an isomorphous series from \( x = 0 \) to \( x = 3 \).

The main mechanism for hydrogen incorporation in silicate structures is through hydrogarnet substitution: \( \text{Si}^{4+} \leftrightarrow 4\text{H}^+ \). That is, protons are arranged in connection with four oxygen anions surrounding tetrahedral Si-free vacancies. The replacement of H for Si atoms was originally observed by Cohen-Addad et al. (1963) via nuclear magnetic resonance and neutron diffraction experiments on the fully hydrated synthetic sample \( \text{Ca}_3\text{Al}_2(\text{H}_4\text{O}_4)_3 \). Afterward, numerous experimental studies on other hydrogarnets have confirmed this process (Aines and Rossman 1984; Cohen-Addad et al. 1967; Foreman 1968; Lager et al. 1989).

The incorporation of hydrous components into NAMs significantly affects their physical and chemical properties, thus modifying their technological applicability. Examples are the hydrolytic weakening of silicate materials for glass technologies (Griggs 1967), and the dielectric loss increase of ceramic substrates used as electronic packaging materials (Shannon et al. 1992). Changes in elasticity are also relevant to the properties of the Earth’s mantle where they can hold relatively large amounts of “water” (Knittle et al. 1992; Mackwell et al. 1985; O’Neill et al. 1993).

Apparently, the hydration capability of garnets is directly related to the Ca content in the dodecahedral sites (X). Indeed, natural occurrences show ugrandites, \( \text{Ca}_3(\text{Al,Fe,Cr})_2(\text{SiO}_4)_3 \), featuring “water” contents up to about 20 wt% (Passaglia and Rinaldi 1984), while pyralspites, \( \text{(Mg,Fe,Mn)}_3\text{Al}_2(\text{SiO}_4)_3 \), stand between 0.01 and 0.25 wt% (Aines and Rossman 1984). The analysis of synthetic samples confirms such differences (Ackermann et al. 1983; Cohen-Addad et al. 1963; Geiger et