

## Hydrogen incorporation mechanism in synthetic katoite-grossular and natural grossular: $^1\text{H}$ static and MAS NMR and first-principles calculation

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The “hydrogarnet substitution” of four H ions for one Si in a tetrahedral site is well known for the katoite-grossular series at high H concentrations. However, the H structural environments in natural grossular with low H concentrations are not well understood. Here we use a combined approach of  $^1\text{H}$  MAS and static NMR measurements (9.4 T) and first-principles GIPAW calculations (using Quantum-ESPRESSO), similar to our recent study on hydrous forsterite [1], to provide new insights on H incorporation in grossular.

Samples investigated include: (1) two  $\text{Ca}_3\text{Al}_2(\text{H}_4\text{O}_4)_3$  katoite samples synthesized hydrothermally at 0.3 GPa, 250 °C for 2 weeks (see [2]), (2) a  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{2.3}(\text{H}_4\text{O}_4)_{0.7}$  hydrogrossular synthesized hydrothermally at 0.1 GPa and 380 °C for 3 weeks, (3) a colorless, transparent natural grossular (~0.1 wt%  $\text{H}_2\text{O}$  by  $^1\text{H}$  NMR) from Jeffrey Mine, Asbestos, Quebec (CMNMC48324, described in [3]). Phase identification was confirmed by powder X-ray diffraction.

The  $^1\text{H}$  static NMR spectra for the synthetic katoite and hydrogrossular are both broad, spanning a frequency range of ca. 100 and 80 kHz, respectively; their MAS NMR spectra are dominated by a broad central band at ca. 1.0 and 2.3 ppm with FWHM of ca. 8.7 and 4.3 ppm (at 30 kHz MAS), respectively, and extensive spinning sidebands. These features are well reproduced by first-principles calculation. The broad peak widths are due to strong  $^1\text{H}$ - $^1\text{H}$  homonuclear dipolar couplings among protons. Four protons are located near the faces defined by the O atoms of the  $\text{O}_4\text{H}_4^+$  tetrahedron. For katoite, dipolar interactions between protons on nearest tetrahedra are significant.

The  $^1\text{H}$  static and MAS NMR spectra of the natural grossular sample show similar features to the synthetic hydrogrossular. Thus they are consistent with similar 4H for 1Si substitution, contrary to previous proposals.

[1] Xue *et al.* (2017) *Am. Mineral.* **102**, 519-536. [2] Geiger *et al.* (2012) *Am. Mineral.* **97**, 1252-1255. [3] Palke *et al.* (2015) *Am. Mineral.* **100**, 536-547.