Computational Details

Let us outline briefly the practical procedure adopted to build the classes of configurations with the CRYSTAL14 code. Starting from the grossular primitive cell, we run a SA-MC sampling of the configurational space (keyword CONFRAND) for each composition n, in order to select the corresponding SICs. This step of the calculation is quite fast and generates an external unit (CONFIGURATIONS.DAT) where the SICs found are listed by the respective ranks. After that, the RUNCONFS option is used to automatically generate the structures of the SICs corresponding to the ranks stored in the external unit. In fact, this procedure works for $1:1$ substitutions only, while the hydrogarnet substitution implies a $1(\mathrm{Si}):4(\mathrm{H})$ ratio. In this case, it was therefore necessary to simulate first a fake $1:1$ substitution in order to identify the involved crystallographic sites, and then build the true structure manually. For this last step, we used fully hydrated katoite as a basis structure, and combined the keywords ATOMREMO and ATOMINSE for removing H and inserting Si in the correct positions. Finally, each SIC structure was fully optimized.