Investigation on the crystal structure of $Co_2CO_3(OH)_2$ by DFT and X-ray diffraction

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The cobalt carbonate hydroxide $Co_2CO_3(OH)_2$ can be used as a precursor in the synthesis of cobalt oxides. This phase can also have a certain interest as a potential immobilizer of the toxic element cobalt. It is considered to belong to the group of the mineral Rosasite, but its crystal structure has not been fully determined. In this work the structure of $Co_2CO_3(OH)_2$ is investigated by Density Functional Theory (DFT) simulations and X-Ray Diffraction (XRD) measurements of synthetic samples that have been obtained via reaction-precipitation from aqueous solutions. Two eventual monoclinic structures -closely related but symmetrically different- have been considered in simulations: (i) based on malachite $Cu_2CO_3(OH)_2$ and (ii) based on Rosasite $Cu_{1.5}Zn_{0.5}CO_3(OH)_2$. Moreover, an hypothetic orthorhombic phase that can be seen as a common parent structure for the two monoclinic phases, and a triclinic phase based on the crystal structure of $Cu_{1.34}Co_{0.66}CO_3(OH)_2$ (mineral Kolwezite) have also been considered. From the DFT simulations carried out in this work it can be deduced that the monoclinic considered phases are two different local minima of the potential energy of $Co_2CO_3(OH)_2$, and are virtually degenerate in energy. However, the orthorhombic and triclinic structures are unstable and converge to the malachite phase after relaxation. The refinement of the XRD data shows that the best fit is obtained using a Rosasite model. However, some features of the XRD pattern are still not well accounted for by this refinement and the residual parameters are poor. The structural relationship between the Rosasite-like and malachite-like can be seen as polytypes and we propose that some level of stacking disorder could explain the misfit of XRD data.