H/D isotope effects in brucite at low temperatures

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ABSTRACT

Joint refinement of powder neutron diffraction data of hydrogenated and deuterated brucite over the temperature range of 10–295 K clearly shows significant isotope effects in the structural parameters. $Mg(OH)_2$ has a 0.31% larger volume than that of $Mg(OD)_2$ at room temperature, which is mostly due to the c-axis expansion of $Mg(OH)_2$ as compared to $Mg(OD)_2$. The isotope effect in the a-axis has the opposite, but smaller, behavior as compared to the c-axis. These differences are slightly enhanced with reduction of the cell volume upon cooling. The temperature dependence of the isotropic atomic displacement parameters (ADPs) with the single site model show that the ADP of the H atom is approximately larger than that of the D atom by the amount expected from the reduced-mass difference, but this difference is not evident with the split site model. Despite the shorter c-axis of the deuterated form, nearest-neighbor $D\cdots D$ distances are longer than the $H\cdots H$ distances, because the O-H distances are longer than the O-D distances, which necessarily places the H atoms closer together by 0.03 Å or more within the interlayer space. This study showcases an example of when a joint Rietveld refinement is ideally suited, by combining data for the deuterated and hydrogenated forms of brucite. The approach reduces the number of least-squares variables, and reduces the systematic errors. It can be a general method to analyze isotope effects in materials studied by neutron diffraction.

Keywords: Rietveld refinement, brucite, neutron diffraction, isotope effect