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Low-temperature crystallography and vibrational properties of rozenite ($FeSO_4 \cdot 4H_2O$), a candidate mineral component of the polyhydrated sulfate deposits on Mars

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Abstract

Rozenite ($FeSO_4 \cdot 4H_2O$) is a candidate mineral component of the polyhydrated sulfate deposits on the surface and in the subsurface of Mars. To better understand its behavior at temperature conditions prevailing on the Martian surface and aid its identification in ongoing and future Rover missions, we have carried out a combined experimental and computational study of the mineral's structure and properties. We collected neutron powder diffraction data at temperatures ranging from 21–290 K, room-temperature synchrotron X-ray data and Raman spectra. Moreover, first-principles calculations of the vibrational properties of rozenite were carried out to aid the interpretation of the Raman spectra. We found, in contrast to a recent Raman spectroscopic study, that there are no phase transitions between 21 and 290 K. We confirm the heavy atom structure reported in the literature (space group $P2_1/n$) to be correct and present, for the first time, an unconstrained determination of the H atom positions by means of high-resolution neutron powder diffraction, and report the complete crystal structure at 290 and 21 K. The anisotropy of the thermal expansion of the lattice vectors is $\alpha_a:\alpha_b:\alpha_c = 1.00:2.19:1.60$ at 285 K. Subsequent analysis of the thermal expansion tensor revealed highly anisotropic behavior as reflected in negative thermal expansion approximately $\parallel\langle 101\rangle$ and ratios of the tensor eigenvalues of $\alpha_1:\alpha_2:\alpha_3 = -1:3.74:5.40$ at 285 K. Lastly, we demonstrated how combining Raman spectroscopy and X-ray diffraction of the same sample sealed inside a capillary with complementary first-principles calculations yields accurate reference Raman spectra. This workflow enables the construction of a reliable Raman spectroscopic database for planetary exploration, which will be invaluable to shed light on the geological past as well as in identifying resources for the future colonization of planetary bodies throughout the solar system.

Keywords: Polyhydrated sulfates, Mars, rozenite, negative thermal expansion, Raman spectroscopy, density functional theory, neutron diffraction, synchrotron X-ray diffraction