Structural and molecular spectroscopic behaviour of the Mg-Mn kieserite solid solution, (Mg,Mn) SO_4 ·H₂O, with relevance to icy satellites of Jupiter and Saturn

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The investigation of the presence of sulfates in our solar system receives growing attention, as these compounds significantly influence melting equilibria on the icy moons of Saturn and Jupiter, leading to the existence of subsurface oceans and even cryovolcanism (Kargel, 1991, McCord et al., 2001). Although higher-hydrated sulfates such as epsomite and mirabilite dominate on their surfaces, it is not excluded that low-hydrated Mg-sulfates, such as kieserite (MgSO₄·H₂O), are also present, as indicated by the results of high-pressure experiments (Kargel, 1991, Nakamura and Ohtani, 2011). Given the significant content of Mn-sulfate in the soluble fraction seen in some carbonaceous chondrites (Frederiksson and Kerridge, 1988), an intermediate composition of kieserite and other Mg-sulfates on the icy moons along the Mg/Mn solid solution series may be expected. The relationship of structural and spectroscopic properties along the entire Mg-Mn kieserite solid solution range is of particular interest, in view of the known differences between both endmembers.

We hereby present first results on structural and lattice parameter changes from single crystal X-ray diffraction data of hydrothermally synthesized material with variable Mg/Mn ratio. Respective FTIR and Raman spectra reveal a slight decrease in the wavenumber positions of the vibrational modes of the SO₄ tetrahedra, as the Mn/Mg ratio progresses towards Mn-dominant compositions. A well-resolved IR absorption band at around 840 cm-1 shows a significant decrease in wavenumber position with increasing Mn-content. The entire Mg-Mn kieserite solid solution shows Vegard-type behaviour, i.e. lattice parameters as well as spectral band positions change along linear trends with increasing Mn content. While the changes in wavenumber position observed for the SO₄ absorption features in the IR spectra are too subtle, the changes in the wavenumber position of the ~840 cm-1 band enable to roughly estimate the Mn/Mg ratio in extraterrestric kieserite from present and future IR remote sensing data as well as in-situ measurements. The narrow bands in Raman spectra with few overlaps make it possible to infer on the Mn/Mg ratio even using the changes in wavenumber position of the sulfate vibrational modes.

As a complication, noticeable changes in the wavenumber position of the 'diagnostic' bands are observed with decreasing temperature. Despite these deviations (which can in addition be compensated by the knowledge of the measurement temperature), one can roughly determine the chemistry of extraterrestric kieserite along the Mg/Mn binary join from vibrational spectra acquired by orbital reconnaissance missions and future lander missions to the icy moons of Jupiter and Saturn.

References:

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