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Raman Spectroscopy of Mars Relevant Minerals at Different Atmospheric, Pressure, and Temperature Conditions

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Abstract

In the scope of the ExoMars mission Raman measurements will be performed with the RLS Spectrometer to identify organic compounds and mineral products as indicators of biological activity [1]. Minerals produced by water related processes as well as igneous minerals and their alteration products will be characterized. Furthermore, in this context it is of interest to assess the influence of the environmental conditions on the Raman spectra. Measurements performed under conditions different temperature or pressure from environmental condition on Earth might have an influence on Raman spectra [1-3]. Here Raman spectra of Mars relevant minerals are presented. The analysis is made in vacuum, and with pressure, temperature, and atmospheric composition corresponding to environmental conditions on Mars and for comparison on Earth.

1. Introduction

The minerals sylvite (KCl), anhydrite (CaSO₄), gypsum (CaSO₄*2H₂O), phlogopite (KMg₃(Si₃Al O₁₀)(F,OH)₂), tremolite (Ca₂(Mg,Fe²⁺)₅Si₈O₂₂(OH)₂), carnallit (KMgCl₃*6H₂O) have been chosen for this study as they are (1) known as weathering or sedimentary products on earth and some of them have already been detected on Mars, (2) easy to prepare for Raman measurements and available in larger amounts, and (3) are perfect indicator minerals for Raman spectra shifts due to changes of ambient conditions [4 - 6].

2. Sample Preparation and Raman Measurements

The samples used for the investigation are cutted in pieces of about $1 \text{cm} \times 1 \text{cm} \times 0.5 \text{cm}$ size with the large faces being plane parallel. For the measurement one plane parallel surface is polished and the sample

is fixed in a cryostat. The samples are first measured under normal laboratory conditions, i.e. 300 K, 1 bar, and Earth atmosphere. After this the cryostat is evacuated and Raman spectra are taken in vacuum. Subsequently measurements are performed in CO₂-atmosphere of 8 mbar and 300K. In a next step measurements are made again in vacuum but 200K, and in Mars-like conditions of 8 mbar CO₂ atmosphere and 200K. In a last step all samples are investigated under normal laboratory Earth conditions again to exclude any irreversible changes in the minerals.

All Raman measurements are performed with a confocal Raman microscope Witec alpha300 R [7]. The Raman laser excitation wavelength is 532 nm. The spectral resolution of the spectrometer ranges between 4 -5 cm $^{-1}$. A Nikon 10x objective was used. The spot size is in focus less than 1.5 μm . The laser power is 1 mW on the sample. This value is expected for the RLS instrument on ExoMars.

The measurements performed in vacuum and under Mars-like conditions are carried out in a modified Oxford cryostat MicrostatHiResII. The cryostat is mounted below the objective of the Raman microscope and the measurements are obtained through a crystalline quartz glass.

3. Results

In Figure 1 the Raman spectra of carnallite are shown in the O-H - streching region between 3200 cm $^{-1}$ and 3600 cm $^{-1}$ for different environmental conditions. The measurements made under normal conditions, under vacuum and CO_2 at 8 mbar do not differ in the position of the Raman band. A change in Raman intensity can be seen for the CO_2 – 8 mbar atmosphere. The Raman band shifts when the temperature decreases to 200K. The band shift is larger for vacuum than for the CO_2 – 8 mbar atmosphere. Furthermore, the Raman band is more

structured for vacuum and 200K. This can be explained with a sharpening of the individual OH – stretching lines possibly due to increased ordering of the water molecules in the crystal lattice [8]. The minerals sylvite, anhydrite, gypsum and tremolite are investigated as well and will be presented.

Figures

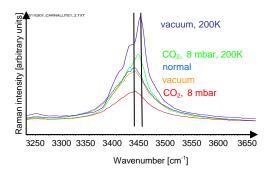


Figure 1: Raman spectra of carnallite in the region between 3200 cm⁻¹ and 3600 cm⁻¹ for different environmental conditions: normal – blue; vacuum - orange; (CO₂, 8 mbar) – red; (vacuum, 200 K) – light blue; (CO₂, 8 mbar, 200 K) – green.

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