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LIBS studies on frozen salt solutions under Martian conditions

S. Schröder (1,2), S. G. Pavlov (1), E. K. Jessberger (3) and H.-W. Hübers (1,2)
(1) Institut für Planetenforschung, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Berlin, Germany, (2) Institut für Optik und Atomare Physik, Technische Universität Berlin, Germany, (3) Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Germany (susanne.schroeder@dlr.de)

Abstract

The capability of laser-induced breakdown spectroscopy (LIBS) to detect and identify salts of different kind in frozen salt solutions was investigated under Martian conditions. The plasma characteristics and thus the resulting spectra and line intensities strongly depend on the laser power density on the sample's surface and on properties of the ice i.e. the opacity and consistency. In this study the focus was on discriminating sulfates from chlorides in ice. Moreover, the capabilities of LIBS for depth profiling of the frozen salt solutions were investigated.

1. Introduction

For the determination of the elemental composition of various materials, laser-induced breakdown spectroscopy has been proven to be a powerful analytical technique. In particular its application in space science to investigate geological surfaces of solar system bodies other than the Earth is of prime interest. As part of the ChemCam instrument on NASA's Mars Science Laboratory (MSL) rover (scheduled for launch in fall 2011), LIBS will be applied for the first time for the in-situ investigation of geological samples on a planetary mission [1]. But also other missions with LIBS as part of the rover's or lander's payload are proposed, including missions to the Earth's Moon, Venus, asteroids or even more distant targets such as icy moons of Jupiter or Saturn e.g. [2, 3, 4].

2. Technique

LIBS is an emission spectroscopy technique and permits rapid multi-element analysis. It relies on ablating material from the target by focusing radiation from a pulsed laser onto the sample's surface. Sufficient laser energy enables the production of a small luminous plasma which can be analyzed spectroscopically. Information about the elemental composition is obtained due to specific atomic or ionic transitions and the appropriate emanating photons resulting in characteristic spectral lines. To obtain the chemical composition of rocks, soils and frozen samples with LIBS in particular for its application on Mars qualitative and quantitative analytical methods have been developed and improved by a number of studies. One attempt to compensate for matrix effects and other factors that influence the plasma composition and properties and thus the LIBS spectra are multivariate analysis (MVA) methods such as principal component analysis (PCA).

3. Results

A set of eight salt solutions consisting of four chlorides and four sulfates with cations of the same kind was prepared with 2 wt% of the appropriate salt in water, degassed, and frozen in small copper containers. The samples were analyzed at a temperature of 200 K. Measurements were performed under Martian atmospheric conditions with an appropriate gas mixture at a pressure of 7 mbar in a dedicated simulation chamber at DLR Berlin. In this laboratory study an infrared Nd:YAG laser was used to generate the plasma at distances < 1 m: 1064 nm wavelength, up to 220 mJ pulse energy, 8 ns pulse duration, 10 Hz repetition rate. For every salt 10 spots were probed and for one spectrum the emission of 20 plasma was accumulated each. Relevant lines for the analysis were identified in the spectral range from 280 nm to 900 nm and PCA was applied, for the whole data set as well as for selected lines only. Clearly detectable lines of the alkali metals (Na, K) and alkaline earth metals (Mg, Ca) allowed for discrimination between salts with different cations. Generally, the strongest sulfur and chlorine lines are hardly detectable in this spectral range, proving clear discrimination between sulfates and chlorides difficult but not impossible when PCA is applied.

Furthermore, the capability of LIBS for depth profiling of the frozen salt salt solutions was investigated. In Fig. (1) the absolute line intensities of the most intense sodium lines at 589.0 nm and at 589.6 nm in the LIBS spectra of NaCl ice obtained with singles shots each are shown. During the LIBS measurements usually some of the water near the surface sublimates and a salt layer develops on top of the sample. This is visible to the unaided eye and also apparent from the depth profiling plots. The intensity of the sodium lines drops rapidly with the number of shots on the same spot whereas the oxygen and hydrogen lines are much less affected and decline less (not shown here) primarily due to the laser drilling into the ice and the accompanying effects. These plots suggest that the spectra obtained with first shots are the most relevant to identify the salts in the frozen solutions when averaging 20 spectra for the PCA.

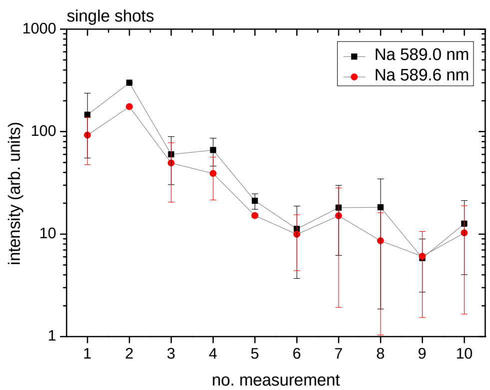

Figure 1: Depth profiling with LIBS on frozen NaCl solution. The plot shows the line intensities of Na 589.0 nm and Na 589.6 nm in the LIBS spectra obtained with single shots ten times on the same position.

Acknowledgements

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References

[1] Wiens, R. C. et al.: Calibration of the MSL/ ChemCam/ LIBS Remote Sensing Composition Instrument, LPSC 42th, Abstract #2370, The Woodlands, Texas, 2011.

[2] Lasue, J. et al.: Applicability of LIBS on the Moon: Elemental analysis of lunar simulants in vacuum, LPSC 42th, Abstract #1165, The Woodlands, Texas, 2011.

[3] Pavlov, S. G. et al.: Miniaturized laser induced plasma spectrometry for planetary in-situ analysis - the case for Jupiter’s moon Europa, Adv. Space Research, in print.

[4] Clegg, S. M. et al.: Venus Geochemical Analysis by Remote Laser-induced Breakdown Spectroscopy (LIBS), LPSC 41th, Abstract #1631, The Woodlands, Texas, 2010.