

INVESTIGATION OF MgCl, MgF, CaCl AND CaF EMISSION IN LIBS FOR THE QUANTIFICATION OF CHLORINE AND FLUORINE IN MARTIAN ATMOSPHERIC CONDITIONS. D.S. Vogt¹, S. Schröder¹, K. Rammelkamp¹, P.B. Hansen¹, S. Kubitza¹, H.-W. Hübers^{1,2}, ¹Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Optische Sensorsysteme, Berlin, Germany. ²Humboldt-Universität zu Berlin, Institut für Physik, Berlin, Germany. (David.Vogt [at] dlr.de).

Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) is an increasingly important tool in the exploration of Mars. The first LIBS instrument in space is the highly successful ChemCam instrument on board of NASA's Mars Science Laboratory, which continues to provide valuable geological data of the Martian surface [1-3]. In 2020, two more missions to Mars that will feature LIBS instruments are scheduled to launch: NASA's Mars 2020 mission with SuperCam [4], the successor of ChemCam, and the Chinese HX-1 mission with the Mars Surface Compound Detector (MarsCoDe) [5].

The detection of chlorine and fluorine in Martian targets has been a challenge for ChemCam due to their low-intensity emission lines in the UV/VIS/NIR spectral range. The detection via molecular emissions of simple molecules that form inside the plasma has been proposed as a way to enhance the level of detection (LOD) for halogens [6]. Molecular emissions of CaCl and CaF have already been useful for the identification of chlorine and fluorine in ChemCam spectra [7]. Their strongest bands are the A-X bands at 618 nm (CaCl) and at 605 nm (CaF). The dependence of the intensities of these molecular emissions on compositional changes of the samples has not yet been investigated extensively, however. We previously reported that the concentrations of both elements inside the plasma were found to have a big influence on the intensity of the molecular bands [8].

The molecular emissions of MgCl and MgF have also been considered as potential signals for the detection of chlorine and fluorine [6]. Their strongest bands are located at 377 nm (MgCl A-X) and at 357 nm (MgF A-X), respectively, which is outside of ChemCam's spectral range, but could be in the spectral range of future LIBS instruments on Mars.

In this study, the molecular emissions of CaCl, CaF, MgCl, and MgF in LIBS are investigated in laboratory studies in simulated Martian atmospheric conditions and in plasma simulations using the equilibrium model. The dependence of the CaCl and CaF emissions on the reactant concentrations is analyzed theoretically based on chemical rate equations in the plasma. The intensities of the MgCl and MgF emissions are compared to those of the atomic emission lines of Cl and F in order to determine whether they can also be used to improve the LOD of the two halogens in samples with a high magnesium concentration. Furthermore, spatially and temporally resolved measurements of the CaCl emission and of the CaF emission are made in order to gain a better understanding of molecular formation in the laser-induced plasma.

Materials and methods: We have examined pure samples of chloride and fluoride salts as well as mixtures of salts of varying composition. $MgCl_2 \cdot 6H_2O$ and MgF_2 were used for the detection of the MgCl and MgF emissions. For the CaCl and CaF emissions, test series were made in which the concentrations of Ca and Cl and the concentrations of Ca and F were anti-correlated, respectively. For the CaCl series mixtures of KCl , K_2SO_4 , and $CaCO_3$ were used, and for the CaF series mixtures of MgF_2 , K_2SO_4 , and $CaCO_3$ were used at varying concentrations. For the spatially resolved measurements, samples of $CaCl_2 \cdot 2H_2O$ and CaF_2 were used as well as one mixed sample of $NaCl$ and $CaSO_4 \cdot 2H_2O$ at a 4:1 ratio.

Two LIBS setups at DLR Berlin were used for this study. The first setup uses an echelle spectrometer (LTB Aryelle Butterfly) to achieve a high spectral resolution of 30-90 pm and a high spectral range of 270-850 nm. An ICCD camera (Andor iStar) detects the LIBS spectrum, allowing for time gating of the

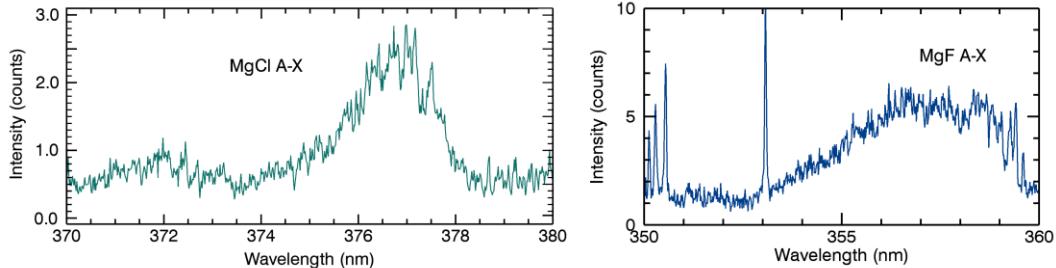


Fig. 1: LIBS spectra of the most intense MgCl band (left) and the most intense MgF band (right).

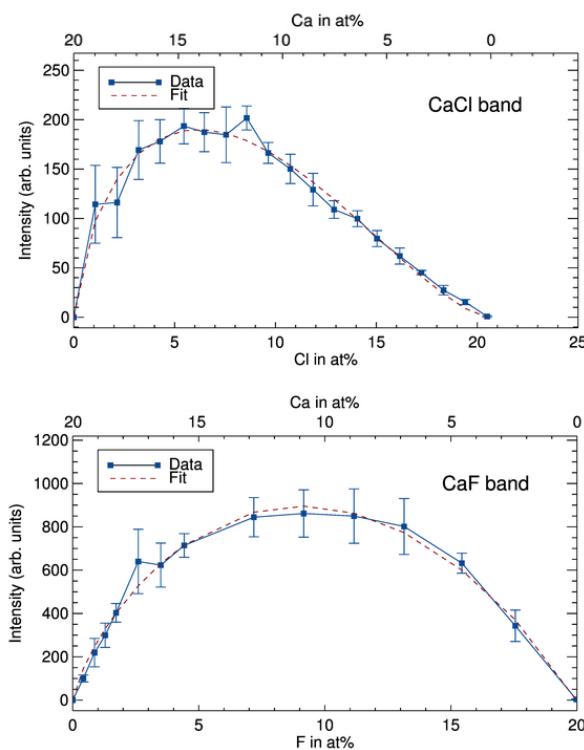


Fig. 2: Top: CaCl band intensity for different Ca and Cl concentrations. Bottom: CaF band intensity for different Ca and F concentrations. Both are fitted by the same reaction model.

signal with a precision of about 10 ns. A Q-switched Nd:YAG laser (Continuum Inlite) with $\lambda = 1064$ nm and a pulse width of 6 ns is used to generate the plasma. The maximum laser energy of 100 mJ/pulse inside the simulation chamber is reduced to 20 mJ/pulse for the measurements in this study with filters in the optical path. The second setup allows for time-resolved plasma imaging and is described in detail by Schröder et al. (this conference).

Results: The MgCl and MgF bands in the LIBS spectra of samples containing MgCl₂ and MgF₂ are very weak (Fig. 1). The Cl(I) line at 837.6 nm and the F(I) line at 685.6 nm are more intense, so that these molecular emissions cannot be used to improve the LOD. They will also likely be too weak to be observed in any Martian LIBS spectra. Equilibrium plasma simulations show that the explanation is a low population density of the excited levels.

In the anti-correlated test series made for the investigation of CaCl, the CaCl band shows a strong asymmetrical behavior despite the symmetrical changes of the Ca and Cl concentrations (Fig. 2 top). The maximum is skewed towards low Cl concentrations and high Ca concentrations, suggesting that the formation of more CaCl at higher Cl concentrations is reduced because of the formation of

CaCl₂ in the low-temperature regions of the plasma. The effect is much weaker in the case of the CaF band intensity (Fig. 2 bottom), which is almost symmetrical around the center at 10 at% Ca and F. This could indicate that the higher dissociation energy of CaF (5.5 eV instead of 4.1 eV for CaCl) leads to a more stable CaF concentration in the plasma. The equilibrium model fails for these results, but our reaction model can be used to describe the curve of the band intensity accurately.

In the spatially resolved measurements of the sample mixed from NaCl and CaSO₄·2H₂O, the CaCl emission appears after about 700 ns (Fig. 3). It is located directly in the plasma center, which is surprising because the plasma center was considered to be too hot for stable molecules. This indicates that the plasma temperature distribution is more complex than initially thought and might be very low at the center in later stages of the plasma, likely because of strong dynamic effects and radiative losses.

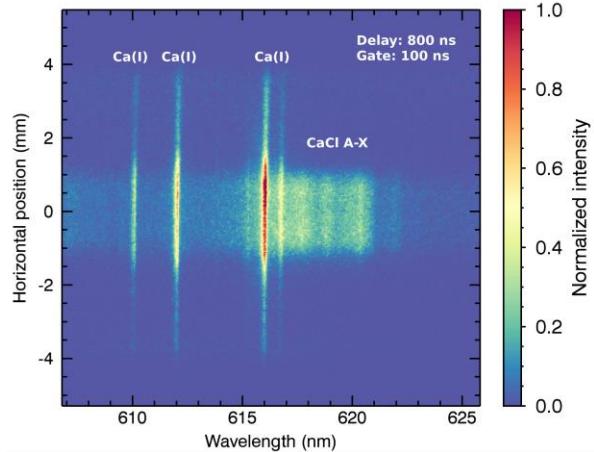


Fig. 3: Spatially resolved spectrum of NaCl and CaSO₄·2H₂O showing the CaCl A-X band and Ca(I) lines.

Conclusion: The CaCl and CaF bands are well-suited for quantification, but the dependence on the reactant concentrations strongly affects the intensity and needs to be considered in calibration curves. The MgCl and MgF bands are not suited for the analysis of Cl and F due to their low intensity. Plasma imaging can offer important insights that improve our understanding of molecular formation in the laser-induced plasma.

References: [1] Maurice et al. 2012. *Space Sci. Rev.* 170: 95–166. [2] Wiens et al. 2012. *Space Sci. Rev.* 170: 167–227. [3] Maurice et al. 2016. *JAAS* 31: 863–889. [4] Wiens et al. 2017. *Spectroscopy* 32: 50–55. [5] Ren et al. 2018. *EPSC 2018: idEPSC2018-759*. [6] Gaft et al. 2014. *Spectrochim. Acta B* 98: 39–47. [7] Forni et al. 2015. *Geophys. Res. Lett.* 42: 1020–1028. [8] Vogt et al. 2018. *Icarus* 302: 470–482.