

VIS – NIR Spectral study of salty ice analogue samples with implications for icy moons

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Introduction: Telescopic and spacecraft observations of Jupiter’s moons surfaces have provided information on their composition, mostly from the spectral analysis of the reflected light [1-4]. Except for Io, the surfaces of these bodies are made of crystalline and amorphous water ice and several highly hydrated salty phases whose nature is currently under debate in the scientific community [1 – 9]. As several potential chemical compositions are relevant for the surfaces of these moons, as much as for other bodies covered with hydrated salty phases, the laboratory work ongoing at the University of Bern intends to enlighten how different salts mixed with water ice in different ways affect the reflectance. We prepared several samples by mixing MgSO_4 , NaCl , MgCl_2 and Na_2SO_4 with ices to better constrain how these components, can form hydrated phases depending on the preparation method, which roughly simulate processes for the production of pristine material at the surface of icy moons. We also investigate the effects of the strong irradiation ongoing at the surface of Jupiter’s moons.

Flash-frozen salty ices: Granular ices have been produced through a flash-freezing process by nebulising droplets into liquid nitrogen with the SPIPA (Setup for the Production of Icy Planetary Analogues from the University of Bern) [10], generating solidified phases of water and salts. This preparation process seeks to simulate the production of particles through an active plume at, or close to, the surface. The water ice itself cannot incorporate salt in its crystal lattice at ambient pressure, contrary to high pressure [11, 12]. Given the temperature of liquid nitrogen, particles solidify quickly forming amorphous or glassy phases of salt and water. This process is described in other science fields [13] and demonstrates to which extent a flash-freezing procedure generates highly complex particles, made of both amorphous and crystalline phases.

Slabs of salty ices: Starting from similar composition but simulating a slow freezing process, slabs of salty ices have been produced with different concentrations of salts, from low to saturated proportions (wt% of salt is varies as a function of the phase diagram of the salt with H_2O). Around 15 ml of solutions were placed in sample holders, covered with a lid adapted to the sample holder and placed in the freezer at 233 K for at least 15 hours. We identify the infrared signature of different salt hydrates, expected to form through slow

crystallisation following their phase diagrams and thermodynamic equilibrium [14]. The ice itself has, therefore, the time to expel salt from its crystal. This procedure could be more relevant for ice produced either inside “hydrological” analogues systems inside ice shells, or at the interface of the ice shell and the global salty ocean. By letting slabs samples sublime slowly in vacuum, absorptions bands related to the hydrated phases appeared.

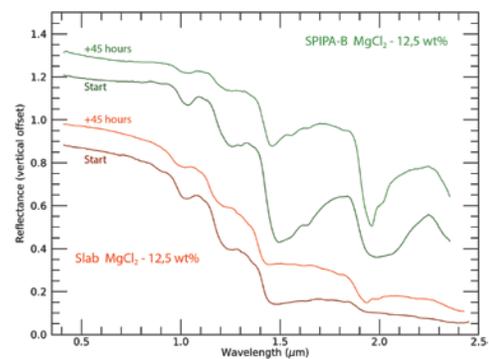


Figure 1: Reflectance spectra of slabs (red) and granular ices (green) made of two different brines containing water and 12.5wt% of MgCl_2 . Green spectra have been positively offset by 0.3.

Figure 1 shows a comparison and evolutions between slabs (red) and granular ice (green) in the case of MgCl_2 . These samples have been produced from initial brines with 12.5wt% MgCl_2 . The two samples have several absorptions bands in common (at 1.46; 1.81; 1.96 μm) previously described as absorption bands of $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ [15] (with n ranging from 1 to 12). The more distorted the absorption complexes at 1.5 and 2.0 μm are, the more hydrated the salts present in the sample are. The differences observed between these spectra are in part due to the particles themselves, in terms of size, but also to the amount of excess water ice removed by sublimation, which is considerably higher with flash-frozen granular salty ices. The production process also generates different hydrated phases and in different proportions. Comparison between the granular flash-frozen particles and the slabs of brines revealed a positive correlation between the degree of hydration and the salt concentration in flash-frozen granular particles for every species tested, at the exception of MgCl_2 which exhibits a contrary behaviour. The slow crystallisation procedure (slabs) is the most efficient to generate a high degree of hydration with lower

salt concentrations. More detailed results will be shown at the conference, for the other chemical species mentioned in the introduction.

Irradiated Ices: F- and M-centres are well-known defects in alkali halides crystals [16, 17], formed through electrons replacement in the crystal lattice. Due to the colouration induced by effect- and M-centres, their relevance and their formation process have been strongly suggested for the surface of Europa [8, 9]. We irradiated salty ices with energetic electrons of 1 and 5 keV, depositing 10^{16} to 10^{17} e⁻/cm², which is equivalent of months to years at the surface of Europa [18, 19]. The ices were produced from liquid solutions with different concentrations of NaCl (5, 10 and 30wt%) either in intra-mixture (ice produced from the salty solution), in inter-mixture (salt and water ice particles are mixed at solid state [10]), or as slabs. Figure 2 shows the different spectra of salty ices after e⁻ irradiations; normalised at their reflectance value at 920 nm (for comparison purposes). Comparing the inter-mixture spectrum to the others, the way the salt is mixed with the ice induces different behaviours through irradiation. Without water ice matrix, the salt reacts to the irradiation and could generate M-centres, as previously described in the literature [8, 9, 17].

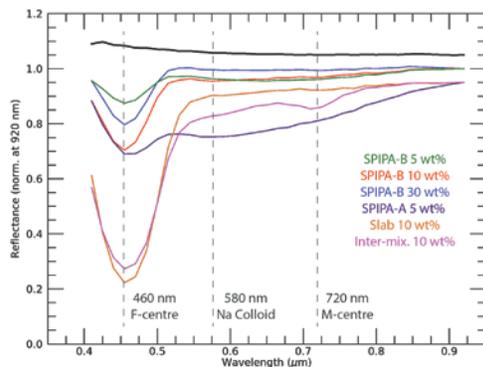


Figure 2: Reflectance spectra of irradiated ices containing 5, 10 or 30 wt% of NaCl (SPIPA-A, Slab and Inter-mix. have been offset by -0.05). The black spectrum is of non-irradiated ice containing 5wt% of NaCl (offset by +0.05). The electron irradiation has been conducted at the energy of 5 keV and current of 1 μ A for 15 minutes.

From SPIPA-B 5wt%, 10wt% and 30wt%, the irradiation is generating stronger alterations in the sample with lower amount of salt (around 10wt%). The efficiency of crystal defect formation is thought to be optimal at low concentrations due to the mobility of crystal defects [20]. Higher concentration favours recombination of crystal defects and their removal due to an increased amount of salt crystals, enhancing the possibility of crystal defects to encounter. Compact slabs are only forming F-centres, which is related to the reduced

mobility of crystal defect (F and H-centres) in colder samples such as compact slabs compare to granular particles under vacuum conditions. The absorption bands present around 580 nm in granular particles are attributed to Na colloids, not suspected to be formed at cryogenic temperatures. Their formation is also related to the mobility of crystal defects and is favoured within warmer samples, such as granular particles.

Summary and Perspectives:

This work demonstrates the major influence of the production method on the spectroscopic properties of salty ices prepared as analogues for the surfaces of the icy moons. The speed and the way the samples crystallise have a strong influence on their structure and composition, and hence on their spectro-photometry. Simulating irradiation conditions occurring at the surface of the icy moons reveals puzzling differences between the behaviours of different samples. Salt concentration, physical properties, and energy of irradiation affect the evolution of the sample through irradiation process leading to the formation of different crystal defects (F and M-centres, Na colloids). These results have implications for the understanding of the surface of Europa, as so far, only the F-centre have been observed, suggesting that compact slab samples better mimic the surface in terms of spectroscopy. Once validated, spectral data will be distributed through the DACE and SSHADE platforms (<https://dace.unige.ch/lossySearch/>; <https://www.sshade.eu/db/bypass>).

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