



VIS-NIR analysis at low temperature and different grain size of ammonium bearing minerals: a tool to improve the knowledge of icy planetary bodies surface.

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Ammonium minerals have been proposed to be present in variable percentage on icy planetary bodies such as Enceladus, Ceres, Pluto and its satellites and their presence is evident also in others celestial bodies. The presence of these compounds is related to the raise of ammonium (NH_4^+) salts from the interior of the icy planetary body, where oceans are likely located, due to cryovolcanism activity mixed with ice. De Sanctis et al. (2020) suggest that the presence of ammonium bicarbonate and/or ammonium chlorides on Ceres's surface is a trace of the recent ascent of deep brine. In fact, some authors (e.g., Castillo-Rogez, 2020) proposed the presence of an early ocean on the subsurface of Ceres as deep brine. The Virgil Fossae on Pluto show evidence of recent cryovolcanism activity and ammonia spectral signature (Cruikshank et al., 2019) revealed by the analysis of data collected by New Horizons from the Linear Etalon Imaging Spectral Array (LEISA) (Schmitt et al., 2017). Recently, several studies (Cook et al., 2018; Dalle Ore et al., 2019) modelled the surface composition of Nix, Hydra and Kerberos, Pluto's moons, using ammoniated salts as end members: NH_4Cl , NH_4NO_3 and $(\text{NH}_4)_2\text{CO}_3$. The identification of these minerals on the surface can give information about internal composition/dynamics and potential habitability of icy bodies. Among the tested samples, several hydrated and anhydrous ammonium compounds undergo phase transitions under specific temperature conditions. For these reasons, these minerals at cryogenic conditions can experience variations in resistivity, electrical conductivity as well as other mechanical properties, that can affect the internal dynamics, cryovolcanism and buoyancy of celestial bodies.

This study focuses on a series of selected minerals, as sulfates, phosphates, aluminates and borates, and is aimed at understanding how (1) different anionic groups, (2) the amount of water, (3) the occurrence of low temperature phase transitions and (4) different grain-size affect the absorption bands parameters of the ammonium bearing minerals. As the experimental data to interpret the remote sensing data, available nowadays for these systems, are usually restricted to small spectral ranges and collected only at room temperature, we performed reflectance spectroscopy analyses in the near-infrared (NIR) region (1-5 μm) in a temperature range from 298K to 60K with specific temperature steps for samples characterised by phase transitions. The reflectance spectra of the samples were measured under cryogenic conditions representative of real planetary surfaces. In addition, ammonium compounds were sieved in three different grain size ranges: 36-80, 80-125 and 125-150 μm . Each grain-size was measured at room temperature. X-ray diffraction analyses were performed on the samples before and after thermal treatments.

We measured natural and synthetic ammonium bearing minerals; sal-ammoniac NH_4Cl , mascagnite $(\text{NH}_4)_2\text{SO}_4$, ammonium bicarbonate $(\text{NH}_4)\text{HCO}_3$, ammonium nitrate NH_4NO_3 , ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, ammonium phosphate monobasic $(\text{NH}_4)\text{H}_2\text{PO}_4$, larderellite $(\text{NH}_4)\text{B}_5\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, struvite $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ and tschermigite $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ using the SHINE spectrogoniometer of the Cold Spectroscopy Facility (<https://cold-spectro.sshade.eu>) at IPAG equipped with a simulation chamber to control the temperature of the minerals. Some of them undergo structural transformations at cryogenic temperature: *i.e.*, mascagnite shows phase transitions at 223 K which involve a changing from space group *Pnam* at room temperature to *Pna2₁*, with ferroelectric behaviour related to a stronger hydrogen bond, whereas tschermigite presents low temperature transitions at 76 K.

Reflectance spectra of anhydrous samples show well defined absorption features in the 1-2.5 μm range due to NH_4^+ groups overtones and combinations. The bands located at 1.3 ($2\nu_3 + \nu_4$) and 1.56 ($2\nu_3$) μm could be useful to discriminate these salts. The reflectance spectra of water-rich samples show H_2O fundamental absorption features, overlapped to the NH_4^+ bands, in the area from 1 to 2.8 μm and over 3 μm the spectra show a minor number of peaks. The parameters (area, depth and FWHM) of several absorption bands change in relation to the low temperature conditions and different grain size. In detail, the low temperature spectra compared to the room temperature ones reveal fine structure displaying more specific and defined absorption bands. The different granulometry affects mainly the bands area and depth. Moreover, we notice as the grain size becoming larger, the value of area and FWHM (full width half maximum) increase. Samples mascagnite $(\text{NH}_4)_2\text{SO}_4$, sal-ammoniac NH_4Cl , ammonium phosphate $(\text{NH}_4)\text{H}_2\text{PO}_4$, tschermigite $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$ and ammonium nitrate NH_4NO_3 are characterized by phase transitions at low temperature and in some cases showed clear and very interesting spectral bands variations during cooling, indicating that a phase transition occurred. In these minerals, the detected phase transitions are characterized by a progressive deepening and shift toward shorter wavelength with an abrupt change in depth of the sensitive bands.

In the analysed temperature range, like that can be found on the surface of large icy bodies, the ammonium minerals undergo different evolutions. In some cases, phase transformations generate important variations in the structural configuration that reflect on the characteristics of the band's parameters and shape. In this scenario, the behaviour of the studied minerals at low temperature is very interesting for the remote sensing identification. These collected cryogenic data, with a carefully analysis of NH_4^+ absorption features, could be used to the detection of these salts on the surfaces of planetary bodies. The presence of ammonium minerals in the ice shell could influence the dynamics of icy satellites, especially if they are subject to phase transformations.

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