The optical constants of gypsum particles as analog of Martian sulfates

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Abstract

Various indications seem to suggest that in the past the Martian climate allowed the presence of liquid water on the surface of the planet. It is therefore reasonable to think that bodies of standing water were once present in basins such as craters or depressions and that evaporite deposits of sulfates could have formed in these basins. The identification of such deposits, which might have survived in some regions of the planet, could confirm the present hypothesis about the ancient climate on Mars. Recent analyses of Mars spectra, obtained by ground-based observations, show bands consistent with sulfate features. If such data have to be interpreted with the aid of synthetic spectra, the knowledge of the complex refractive index of some sulfate is necessary. In this work we present the optical constants of submicron particles of gypsum (a typical hydrate–sulfate very common on Earth), derived by means of the dispersion theory from transmission spectra. We have performed the calculation of the optical constants in the wavelength range 2–70 µm, also in view of the wide spectral range covered by the Planetary Fourier Spectrometer (PFS) on board of the ESA space mission Mars Express. The data have been compared with optical constants obtained by other authors from reflectance measurements of particulate samples.

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1. Introduction

The ancient Martian climate was probably very different from the current one. Now, Mars is an arid and cold desert with an annually averaged surface temperature close to 210 K and an atmospheric pressure of about 6 mbar. However, climatic models suggest the possibility that, in the past, the surface temperature and the atmospheric pressure were high enough to allow a stable presence of liquid water on the surface (Pollack et al., 1987; Forget and Pierrehumbert, 1997; Yung et al., 1997). In particular early Mars may have experienced episodes of warmer and wetter climate with a thicker atmosphere providing a strong greenhouse effect and a higher geothermal heat flux (Pollack et al., 1987; Fanale et al., 1992; Squyres and Kasting, 1994). This hypothesis is supported by remote sensing images which show the presence, on the Martian surface, of interesting geomorphic features such as dendritic channels, apparently carved through slow erosion by water running across the surface (Masursky et al., 1977; Malin and Carr, 1999). These fluvial valleys are very common in the southern highlands of the planet and debouch in basins, such as depressions or impact craters, which possibly hosted paleolakes (Goldspiel and Squyres, 1991; Cabrol and Grin, 1999). If greenhouse warming was important, then many of the atmospheric constituents, such as the volcanically outgassed SO2 (Fanale et al., 1992), have since been lost. In particular it might have been dissolved in water forming bisulfate complexes, possibly leading to the formation of sulfates by means of evaporitic processes. In this scenario sulfates could therefore play a crucial role. Their presence on the Martian surface, particularly in sites such as depressions and craters, could strongly indicate the past existence of water bodies and a thicker atmosphere on Mars. Obviously this may have very important implications on the possibility that life developed on Mars during that

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period (McKay and Stoker, 1989; McKay et al., 1996). Unfortunately, the search for sulfates on Mars has not given a clear answer so far. From a spectroscopic point of view there are not compelling evidences for these materials, in spite of many observations in the near-IR to mid-IR spectral regions, where the strongest vibrational fundamental and overtone bands from sulfur-bearing anions occur (Burns, 1970; Gaffey et al., 1993). Blaney and McCord (1995), by means of ground-based observations, detected an absorption feature near 4.5 μm, interpreted as an SO$_2^-$ overtone band of sulfates in the Martian surface and airborne dust. In addition other spectroscopic observations also pointed out sulfates as likely components of the bright regions (Bishop and Murad, 1996). Pollack et al. (1990) used the Kuiper Airborne Observatory to obtain high-quality spectra in wavelength regions that cannot be observed from the ground. These data showed evidences for spectral features (near 8.7 and 9.8 μm) due to sulfates in the airborne dust, even if the specific mineralogy could not be identified. On the other hand, recent detailed petrographic analyses of the SNC meteorites, thought to be samples of the Martian crust and mantle delivered from Mars to Earth by impacts, have revealed traces of water-precipitated minerals, including sulfates (Goody and Muenow, 1986; Gooding, 1992; McSween, 1994). These are consistent with the in situ elemental analysis made by spectrometers onboard Viking and Pathfinder which have detected significant amounts of sulfur in the Martian soil (Toulmin et al., 1977; Wanke et al., 2001) and with models suggesting sulfates as the cementing agent in the Martian duricrust (Toulmin et al., 1977; Clark and Van Hart, 1981; Bishop, 2001). However, no instrument orbiting around Mars has made a definite identification of sulfates yet. In fact, the Thermal Emission Spectrometer (TES), on board of Mars Global Surveyor, has set only an upper limit of about 15% to the amount of these minerals (Christensen et al., 1998; Bandfield, 2002).

In order to understand the climatic evolution of the planet it would be therefore important to collect new remote sensing data and to continue the spectral search for sulfates in the current databases (i.e. IRIS, TES, THEMIS). The detection of sulfates will be possible only by means of a systematic laboratory study of candidate materials as constituents of the Martian dust. In general, however, it is impossible to directly compare the laboratory data with the remote sensing ones, especially in the thermal range. This is because an appropriate radiative transfer model is necessary to take into account the mutual influence of the surface emission and the contribution of atmospheric dust and gases. In this context the knowledge of the optical constants of sulfates particles may be useful to interpret remote sensing data. In fact they are needed to perform theoretical studies and numerical models of the atmosphere and surface of Mars, since they provide the description of the interaction between the matter and the electromagnetic radiation taking into account the electronic and vibrational transitions for every wavelength. It is important to point out that the extinction spectra of particles, like those present in the Martian environment, can be better reproduced using optical constants directly obtained in the laboratory for particulate materials of the appropriate size. In fact, particular caution must be exercised in extrapolating laboratory results concerning bulk samples to physical conditions where particles smaller than the wavelength are expected to occur (Bohren and Huffman, 1983; Orofino et al., 1998, 2002).

Gypsum is a sulfate mineral very common on Earth and for this reason it has been chosen for the present laboratory study. In particular we have focused on the mineralogical species named selenite. Here we present the results of our calculations performed in order to derive the optical constants of selenite submicron particles in the 2–70 μm spectral range. Other sulphates optical constants have been also obtained from reflection measurements by Aronson et al. (1983) and Roush (1996) for bulk samples of gypsum and fibroferrite respectively. With the same technique Long et al. (1993) have also obtained optical constants for bulk gypsum as well as for pressed pellets of randomly oriented gypsum grains.

In the following sections we briefly describe the experimental method and compare our result with those obtained by Long et al. (1993) for particulate gypsum sample. Then we report some discussions and conclusions.

2. Derivation of the optical constants

Gypsum is an hydrated calcium sulfate (CaSO$_4$·2(H$_2$O)), characterized by a monoclinic cell. A sample of selenite, the monocrystalline mineralogical species of gypsum (provided by WARD’S, USA), has been chosen as target of our analyses. Coarse grains obtained from the bulk selenite sample have been ground by means of an agate mill for 16 h in order to obtain submicron particles. In general grinding process can change the structure of the sample, dehydrating it because of the heating due to friction. In our case, however, the grinding is produced by the vibration of small agate spheres inside the sample which fragment the grains by impact without a large amount of friction. For this reason only in a few cases we experienced appreciable changes in the structure of the samples caused by the grinding process. This is certainly not the case for gypsum since it is very friable (hardness parameter ≈2). This property also explains the lack of differences in grain size by increasing the grinding time.
A qualitative elemental analysis has been performed by means of a Philips XL 20 scanning electron microscope equipped with EDX detection system, both before and after grinding, in order to check for impurities. This analysis has shown the absence of detectable atomic species different from those present inside the selenite lattice. SEM image analysis, performed to check the characteristic grain size, has shown that the sample is composed by clusters of submicron particles as a well as single, isolated grains, as reported in Fig. 1. The characteristic size of these grains is of the order of 0.1 µm. Transmittance spectra of selenite particles have been recorded in the wavelength range 2–70 µm with 2 cm⁻¹ in resolution by means of a Perkin–Elmer Spectrum 2000 FT-IR spectrometer. The infrared transmission spectroscopy has been performed by means of the usual pellet technique (Koike et al., 1980) using both potassium bromide (KBr) and cesium iodide (CsI) as transparent matrices in which selenite grains have been dispersed. A first comparison between the spectra showed that the continuum at short wavelengths is generally more regular in KBr than in CsI. On the contrary, the long wavelength side of the spectra cannot be analyzed using KBr, because this material is not sufficiently transparent beyond about 25 µm. For this reason we recorded the near-medium infrared spectra (2–27 µm) of selenite using KBr as matrix and the medium-far infrared spectra (14–70 µm) using CsI. The spectra obtained in the two matrices overlap in the common spectral range so that the whole spectra of selenite grains were then obtained combining the two spectra without any kind of normalization.

The grain size of our selenite powder has been determined in order to verify the validity of the Rayleigh limit (i.e. 2πa ≪ λ, where a is the particle radius and λ the wavelength of the radiation). In the present calculations such a condition is satisfied in the whole spectral range of interest. We also assume isolated spherical grains. SEM images of our samples, reported in Fig. 1, show the presence of elongated clusters, composed of smaller particles having spheroidal shapes. We expect, however, that during the pellet production needed for the IR spectroscopy, these clusters are disaggregated, resulting in isolated grains dispersed over the matrix, as suggested also by Bohren and Huffman (1983).

Using the transmittance of a sample of very small and nearly spherical grains (with radius a ≪ λ) embedded in a transparent matrix it is possible to derive the ratio $Q_{\text{abs}}/a (\equiv Q_{\text{ext}}/a)$ between the absorption (or extinction) efficiency factor of a particle and its radius. Such a quantity can be linked, using both Mie and the dispersion theory (Bohren and Huffman, 1983), to the parameters of $N$ Lorentzian oscillators by means of the relation:

$$\frac{Q_{\text{abs}}}{a} \approx \frac{4\alpha}{c} \sqrt{\epsilon_m} \sum_{j=1}^{N} \frac{F_j \gamma_j \omega}{(\omega_j^2 - \omega^2 + \gamma_j^2 \omega^2)}$$

where $c$ is the velocity of light in vacuum, $\epsilon_m$ is the dielectric constant of the matrix, $\omega$ is the angular frequency, while $\omega_j, \gamma_j$ and $F_j$ are the three fundamental parameters of the $j$th oscillator. In particular $\omega_j$ is the eigenfrequency, $\gamma_j$ is its damping constant, and $F_j$ is a parameter connected with the plasma frequency strength $\omega_{p,j}$ by means of the relation:

$$F_j = \frac{1}{3} \omega_{p,j}^2.$$  

A semi-empirical procedure of nonlinear fit applied to the spectrum of $Q_{\text{abs}}/a$ can be used to determine the $3N$ values of the oscillator parameters $\omega_j, \gamma_j$ and $F_j$. The Clausius–Mossotti relation (Bohren and Huffman, 1983),

$$\frac{\bar{\epsilon} - 1}{\bar{\epsilon} + 2} - \frac{\bar{\epsilon}_V - 1}{\bar{\epsilon}_V + 2} = \sum_{j=1}^{N} \frac{F_j}{\omega_j^2 - \omega^2 - i\gamma_j \omega},$$

allows derivation of the dielectric function relative to the matrix $\bar{\epsilon}$ and hence the absolute dielectric function $\epsilon = \epsilon' + i\epsilon''$. In Eq. (3) $\bar{\epsilon}_V = \epsilon_V / \epsilon_0$ is the dielectric function relative to the matrix in the visible, evaluated by means of the absolute dielectric constant of the matrix ($\epsilon_0$) and that of the material ($\epsilon_V$). In the present work we use the value $\epsilon_V = 1.975$ derived by Long et al. (1993) for their particulate gypsum sample. Finally, the

Fig. 1. SEM images of the selenite sample at different magnifications. In the left panel it is shown a wide view of the submicron grains, while the right one shows a grain which is a cluster of smaller particles.
complex refractive index of the material under examination can be determined using the equations:

\[
\begin{align*}
n^2 &= \frac{1}{2} \left[ \sqrt{(\varepsilon' - \varepsilon''^2) + \varepsilon'} \right], \\
k^2 &= \frac{1}{2} \left[ \sqrt{(\varepsilon' + \varepsilon''^2) + \varepsilon'} \right].
\end{align*}
\]

3. Results and conclusions

The optical constants of our small selenite grains have been obtained starting with a number of oscillators (13) equal to that of the bands present in the experimental extinction spectrum and then adding further oscillators in order to improve the best fit of the spectrum. This procedure was stopped at the 20th oscillator since the addition of another one produces a percent decrease of the chi-squared which is less than half of the average error of the experimental data. In this way it is possible to fit the experimental spectrum (both continuum and bands) with enough accuracy while limiting, at the same time, the number of free parameters and, consequently, the computation time. The best-fit parameters are listed in Table 1.

In Fig. 2 it is shown the comparison between the experimental extinction spectrum of submicron selenite grains and the theoretical one obtained with Mie theory using the optical constants calculated in this work. The figure also shows the theoretical spectrum obtained with the same theory by using the optical constants derived by Long et al. (1993) for gypsum samples consisting of pellets of pressed grains. These samples are in between bulk material and our particulate samples, consisting of isolated grains dispersed in a transparent matrix. As it can be seen in Fig. 2 the semi-bulk optical constants obtained by Long et al. (1993) give a very poor fit to the laboratory extinction spectrum. We have also checked with a continuous distribution of ellipsoid (CDE – Bohren and Huffman, 1983) but even in this case the semi-bulk optical constants fail to reproduce the experimental spectrum. Due to the generality of the CDE distribution, in which all the shapes (from disks to needles) are equally probable, the negative result of this check strongly suggests that the semi-bulk optical constants fail to reproduce the laboratory extinction spectrum of gypsum grains, regardless the scattering theory used to treat the actual grain shape. We conclude that only our particulate optical constants are able to fit the laboratory spectrum of submicron selenite grains.

The values of the real \((n)\) and imaginary \((k)\) part of the refractive index of our gypsum grains are reported in Fig. 3, where there are also shown the same quantities

\[
\begin{align*}
(n_0 = 1.975 - i\gamma, \text{Long et al., 1993}).
\end{align*}
\]
derived by Long et al. (1993) for semi-bulk gypsum samples. It is difficult to assess the errors both on the real and the imaginary part of the refractive index. In fact they can be derived from a fitting procedure able to reproduce the measured extinction efficiencies within their relative experimental errors. These are usually due to two main causes: the uncertainty on the total mass of the embedded particles and the differences in the spectral behavior of the embedding matrix relative to different samples. Since these experimental errors, depending on the wavelength range, affect in different extent the un
samples. It is difficult to assess the errors both on the derived by Long et al. (1993) for semi-bulk gypsum samples. According to Huffman (1977) and Bohren and Huffman (1983), possible discrepancies can occur, for some materials, between the optical constants valid for bulk samples and those valid for submicron particles. These discrepancies are due to intrinsic properties linked for example to the surface modes which occur in small particles \( 2\pi a/\lambda < 0.1 \) and are often disregarded in the literature. The same reasons can also explain the differences between the optical constants concerning compressed and isolated particles. The fact that in the case of gypsum these discrepancies between the two sets of data (concerning compressed and isolated particles) are quite remarkable must be taken into account when a proper use of the optical constants has to be done.

This work is part of a long-term team effort by the Lecce group, which aims at providing important laboratory knowledge related to optical constants of minerals. Such data are very scarce in the literature, but are essential in the framework of spectral modeling, in particular to invert and deconvolve spectra of the Martian surface and aerosols. In this respect, such data will be needed for the interpretation of future observations by the spectrometers on-board Mars-Express (PFS and OMEGA) and other spacecraft, and are actually also useful for the reinterpretation of past and present data such as TES and IRIS on MGS and Mariner 9 respectively.

In the next future we plan to increase the quality of our gypsum particulate samples by selecting single submicron grains using techniques such as sedimentation. Then we will check the size distribution of the new samples in order to measure the average size of grains in a quantitative way.

Next step will be the use of other spectroscopic techniques (such as reflectance) to perform detailed comparison between optical constants obtained for samples in different physical conditions.

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References


