

GRAIN-SIZE INFLUENCE ON THE MID-INFRARED SPECTRA OF THE MINERALS

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Abstract. Measurements of spectral emittance at wavelengths from 5 to 25 μm were carried out for various particulate rocks and minerals (granite, calcite, talk) in dependence on particle size. The experimentally found variation of spectral features with particle size is discussed in terms of photon's mean free path and its dependence on particle size in the wavelength regions characterized by normal and anomalous dispersion, respectively. Moreover, a sample consisting of fine- and coarse-grained material was investigated in order to estimate the chance for mineral identification at conditions relevant to remote sensing of planetary objects. The mixture spectrum comprises characteristic features of both grain size fractions. This implies that the mineralogical composition of the fine-grained fraction also should be accessible by use of high-sensitive spectrometers.

1. Introduction

Remote sensing in the infrared region provided the major part of our knowledge about the mineralogy and petrology of airless Solar System bodies, and therefore crustal composition and genesis. Especially the large amount of characteristic information in the middle infrared region is very useful for mineral identification. The mid-infrared region has proved to be rich in spectral information for silicate minerals because even the highest-frequency fundamentals, the antisymmetric silicon-oxygen stretching vibrations, occur in the wavelength region from 8 to 12 μm .

Till now, however, this potential was used rather scarce for remote sensing of planetary objects. Most airless planetary objects have their surfaces covered with a regolith of fines, which is produced by the cumulative effect of meteoroid bombardment (Dollfus, 1984). For a object covered with small particles, however, the emitted radiation is strongly influenced by scattering characteristics of the particles, and hence the resulting emittance spectrum depends on the particle size. Studies of the emission behaviour of particulate minerals have shown that the contrast of the major vibrational features ('reststrahlen' bands) is lost as the particle size is reduced (Hunt and Vincent, 1969; Conel, 1969). In particular this loss of spectral contrast prevented the extensive use of mid-infrared spectroscopy for remote sensing of planetary surfaces. In the recent years, however, high-sensitivity measurements coupled with sophisticated data processing and the development of new detector arrays on the basis of cooled $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ semiconductor materials have reawakened the interest in the use of emittance spectra for compositional analysis of planetary surfaces (Kahle and Goetz, 1983; Salisbury and Easters, 1985).

The purpose of this work is to present some measurements of spectral emittance

of particulate minerals carried out with laboratory equipment, to explain the changes of emittance spectra observed for various particles sizes, and to discuss the significance of these results for application in remote sensing.

2. Experimental

Samples of granite, calcite, and talk-slate were used for experiments. All prepared samples were obtained from Forschungsinstitut für Aufbereitung, Freiberg, G.D.R. The 0–250 μm -samples were produced in a dry screen ball mill. Samples below 20 μm were deposited from air elutriation, whereas the material with particles greater than 20 μm was deposited through sieves of appropriate sizes (screen classifying). For spectral measurements the samples were sifted into a 3-cm-diameter by 5-mm-deep cup-shaped sample holder made of aluminium. The measurements were carried out with a Fourier transform infrared spectrometer IRF 180. Using the spectrometer and an emission attachment, the spectral emittance of the powders was measured at atmospheric pressure in the wavelength range from 5 to 25 μm with a resolution of 8 cm^{-1} for a constant sample temperature of 340 K. The reference black-body has concentric V-shaped grooves on its surface and consists of black-painted aluminium. Its emittance at 10 μm wavelength is higher than 0.99.

With σ denoting the wavenumber, T the temperature, $a(\sigma)$ the instrumental responsivity, $\epsilon(\sigma)$ the spectral emittance of the sample, and $B(\sigma, T)$, $B_d(\sigma, T)$, $B_{su}(\sigma, T)$ the spectral radiances of black body, detector and surrounding, respectively, the total spectral radiance $S_s(\sigma, T)$ measured by the spectrometer is given by

$$S_s(\sigma, T) = a(\sigma) \{ \epsilon(\sigma) B(\sigma, T) + [1 - \epsilon(\sigma)] B_{su}(\sigma, T) - B_d(\sigma, T) \}. \quad (1)$$

If we assume that the black-body at the temperature T has a radiance $B(\sigma, T)$ according to Planck's radiation law, the total spectral radiance $S_{bb}(\sigma, T)$ measured for the black body can be written as

$$S_{bb}(\sigma, T) = a(\sigma) [B(\sigma, T) - B_d(\sigma, T)]. \quad (2)$$

Preliminary measurements provided that the radiances of both surrounding and detector can be approximated by the radiation of a black body at room temperature; i.e., $B_{su}(\sigma, T) = B_d(\sigma, T)$. Therefore, the spectral emittance of the sample can be obtained from

$$\epsilon(\sigma) = S_s(\sigma, T)/S_{bb}(\sigma, T). \quad (3)$$

3. Results

The emission spectra of granite are shown in Figure 1 for five different particle sizes between 0 and 630 μm . The principal feature at about 8.5 μm is the reststrahlen band corresponding to the silicon-oxygen stretching mode. This feature and the bands at about 12.2 μm and between 20 and 25 μm can be assigned to quartz.

In the following, the term 'spectral contrast' is used to characterize the strength of a spectral feature with respect to its surrounding. It denotes the absolute difference of the values of the emittance in the band maximum (or minimum, respectively) and in the baseline of the feature. In the emission spectra of granite the spectral contrast of the features is lost as particle size decreases. The band at $8.5 \mu\text{m}$ is detectable even for the smaller grain size, but it appears as a broad, very shallow trough. For the present experimental conditions most features show this behaviour.

Figure 2 shows an emission spectrum of calcite powders for five graduated particle sizes in the range from 5 to $800 \mu\text{m}$. The features occurring at 6.7 , 11.5 , and $14 \mu\text{m}$ are typically for the CO_3^{2-} -group. The $6.7 \mu\text{m}$ -band (ν_3^{a} -antisymmetric stretch of the CO_3^{2-} -group; antiphase mode) demonstrates the above-mentioned decrease of spectral contrast as particle size is reduced. Additionally, striking emission peaks are formed for small grain sizes (below $125 \mu\text{m}$), as already noted by Hunt and Vincent (1969). The minimum found at $11.4 \mu\text{m}$ in the spectrum of the coarsest sample (ν_2 out-of-bending of the CO_3^{2-} -group) appears as a peak for the 63 – $125 \mu\text{m}$ -sample. It becomes more pronounced as grain size decreases. Compared with the minimum at $11.4 \mu\text{m}$, the emission maximum is shifted to longer wavelengths. The feature at $14 \mu\text{m}$ (ν_4^{a} in-plane-bending of the CO_3^{2-} -group; antiphase mode), that appears as a small, barely discernible maximum for the 180 – $800 \mu\text{m}$ -fraction, becomes gradually intensified as particle size is reduced. All the discussed peaks are found also for other carbonate powders, as dolomite and magnesite. Therefore, they can be used to identify carbonates in a mixture of fines. The feature between 13 and $14 \mu\text{m}$ can be used to distinguish different carbonates; for magnesite e.g. it occurs at $13.3 \mu\text{m}$, for dolomite at $13.7 \mu\text{m}$.

As can be seen from Figures 1 and 2, broad, shallow maxima are formed at $7.5 \mu\text{m}$, and in the range from 5.6 to $7.2 \mu\text{m}$, respectively. They are combined with a decrease of emittance at the short-wavelength flank of these features, if particle size is reduced.

Figure 3 presents emission spectra of talk for various grain sizes. The characteristic features at about $9.5 \mu\text{m}$, $14.7 \mu\text{m}$, and in the range from 18 to $25 \mu\text{m}$ can be assigned to the talk itself. The bands at 6.4 and $11.3 \mu\text{m}$ indicate occluded carbonates, as could be confirmed by infrared transmission spectra. The reststrahlen feature of the talk powder at $9.5 \mu\text{m}$ shows highest contrast for particle sizes between 50 and $63 \mu\text{m}$. This is due to an increase of talk concentration with decreasing particle size. Because the talk concentration is lower in the coarser samples, the talk feature shows a decrease of spectral contrast as particle size rises. For grain sizes below $63 \mu\text{m}$ the contrast of most features decreases with particle size in the well-known way; features become barely discernible or they disappear. Quite different is the behaviour of the carbonate band at $11.3 \mu\text{m}$: It appears as a minimum for the largest grain size and changes over to a relatively pronounced maximum as particle size is reduced. Such behaviour was already discussed for other carbonates. In the wavelength regions without any feature, the emittance decreases with particle size.

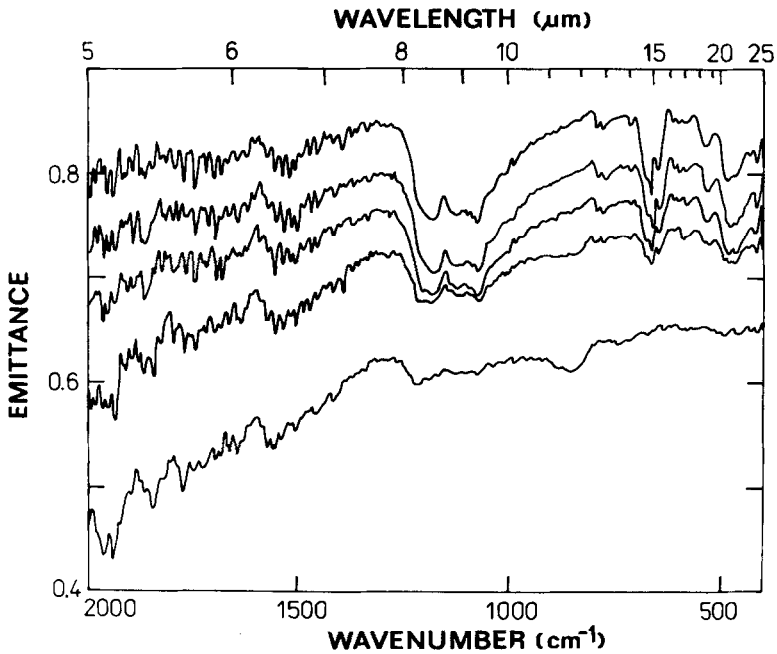


Fig. 1. Spectral emittance of particulate granite samples (place of finding: Dohna (near Pirna), G.D.R.). Grain sizes (curves from top to bottom): 500–630 μm , 200–500 μm , 100–200 μm , 45–100 μm , 0–45 μm .

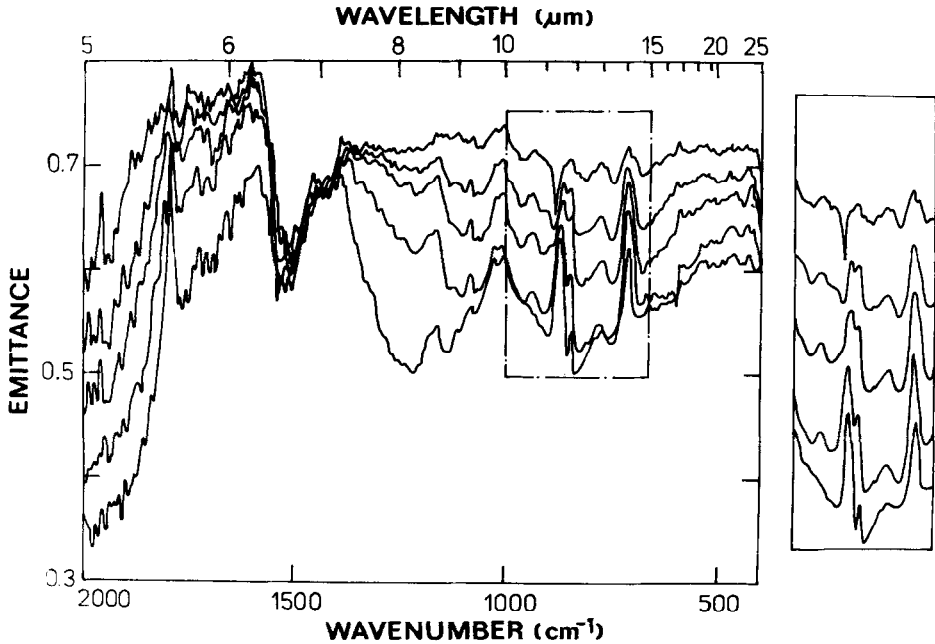


Fig. 2. Spectral emittance of particulate calcite samples (from local deposits). Grain sizes (curves from top to bottom): 180–800 μm , 63–125 μm , 40–63 μm , 32–40 μm , 0–10 μm . For the marked wavelength range, at right each spectrum has been offset for clarity.

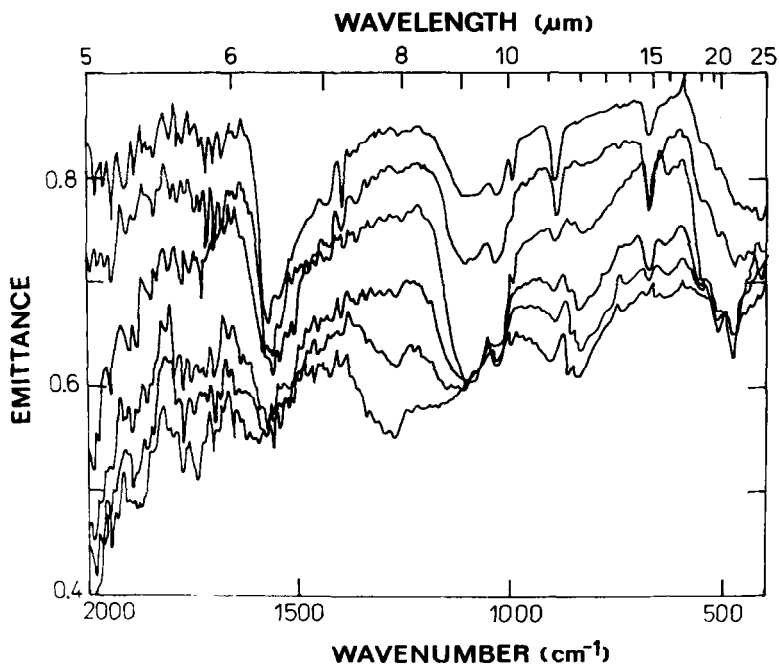


Fig. 3. Spectral emittance of particulate talk samples (talk-slate from Brenner-pass, Austria). Grain sizes (curves from top to bottom): $> 250 \mu\text{m}$, $125\text{--}250 \mu\text{m}$, $50\text{--}63 \mu\text{m}$, $40\text{--}50 \mu\text{m}$, $5\text{--}10 \mu\text{m}$, $0\text{--}5 \mu\text{m}$.

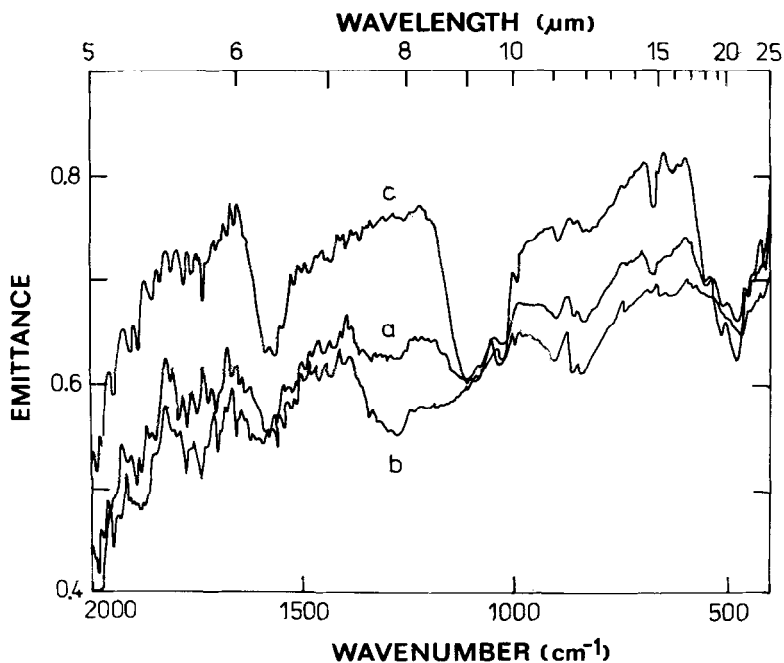


Fig. 4. Spectral emittance of a talk sample comprising equal volume parts (50%) of the grain size fractions $0\text{--}5 \mu\text{m}$ and $50\text{--}63 \mu\text{m}$ (curve a). Emission spectra of both components - $0\text{--}5 \mu\text{m}$ (curve b) and $50\text{--}63 \mu\text{m}$ (curve c) - for comparison.

Figure 4 shows the emission spectrum for a talk sample obtained by mixing equal volume parts of different grain sizes (0–5 μm , and 50–63 μm , respectively). The spectra of the two fractions are shown for comparison. Evidently, the spectrum of the mixture reveals not only the troughs in emittance which are typically for the coarser fraction, but also the emission maxima typically for the fine powder fraction. This demonstrates that the conditions for mineral identification are not appreciable worsened by the presence of the fines.

4. Discussion

The emission spectrum of a polished inorganic solid is readily related to the material's optical constants n (refractive index) and α (absorption index). The spectrum of a particulate sample depends on further quantities, especially particle size and porosity. Therefore, it can appear quite different for various particle sizes and porosities. In the following it is attempted to explain the emission spectrum as a function of particle size. For the sake of clarity, two spectral ranges are discussed separately.

At first, the wavelength range characterized by normal dispersion (i.e. $dn/d\lambda < 0$, with λ for wavelength) is considered. Because the material's absorption index there is rather low and nearly constant, the emission spectrum of a massive or coarse-grained sample does not show any feature in this wavelength region. The decrease of emittance with particle size, proved by the experiments, is explained by an increasing number of interfaces: With decreasing particle size, each photon generated in a certain depth beneath the sample's surface strikes on a rising number of interfaces before escape from the surface layer. Thus, the photon's mean free path decreases, and in this way the probability that photons can escape through the surface layer. This is resulting in a lower emittance.

Emission spectra of particulate material often show broad, shallow maxima at wavelengths below 5 μm , usually combined with a more pronounced decrease of emittance at their short-wavelength flanks. These maxima are related to the Christiansen wavelengths of the material, i.e. those wavelengths where the refractive index of the particles equals that of the surrounding medium (air). Because a particulate sample behaves more transparent at the Christiansen wavelengths than at the others (due to the 'vanishing' interfaces), just for these wavelengths an increased probability results for photon escape to the surface of the sample, and thus a higher emittance. The decrease of emittance found experimentally (for the finest granite powder below 5.6 μm) corresponds very well to the Christiansen wavelengths. They are 7.5 μm for granite (Logan and Hunt, 1970), and about 5.6 μm for calcite, as can be derived from the published optical constants of calcite (Onomichi *et al.*, 1971). The contrast of the Christiansen features becomes intensified as particle size, packing density, background temperature, or pressure decrease (Logan and Hunt, 1970). At atmospheric pressure the feature is hardly discernible as a peak even for the finest powders. Hence, for the experimental conditions used, often only the decrease of emittance at the short-wavelength flank of the Christiansen feature can be detected.

At next, the wavelength ranges characterized by anomalous dispersion (i.e. $dn/d\lambda > 0$) are considered, where both n and α are strongly changing. At these wavelengths the absorption index α becomes very large, and therefore marked minima of emittance appear in the spectrum of a massive or coarse-grained sample (reststrahlen features). As particle size decreases, the contrast of most reststrahlen features decreases too, but for some features the original minimum is inverted into a gradually increasing emission maximum. As will be shown in the following, both modifications result from the same effect of particle size and can be explained in terms of a changed mean free path of generated photons. In the anomalous dispersion wavelength range only photons from a thin surface layer of the sample will be emitted on account of the rather high absorption index. As particle size is reduced, in the anomalous dispersion wavelength range the photon's mean free path *increases* due to (i) the shorter geometric path through the particles and therefore reduced absorption, (ii) the increased porosity of the fine-grained sample, caused by adhesion of small grains (Salisbury and Easters, 1985). This increase of the photon's mean free path L enhances the emittance for decreasing particle size and is just opposite to the previously discussed *decrease* of L (and emittance) occurring in the normal dispersion wavelength region. Just these opposite dependencies of the photon's mean free path on the particle size, occurring within and outside of the reststrahlen range, cause the usually observed decrease of spectral contrast as particle size is reduced. An emission maximum will be formed if the above-mentioned trends cause that L has a higher value in the reststrahlen range than in the neighbourhood of the feature (range of normal dispersion).

Of course, the proposed explanation of the particle size effect on the emission spectrum is only a rough qualitative model till now and has to be checked by quantitative calculation. Nevertheless, it seems to be advantageous compared with former attempts for explaining the influence of particle size and porosity. Vincent and Hunt (1968) explained the particle size influence on the spectral contrast by the varying amounts of specular and volume reflectance components. This, indeed, qualitatively explains decreasing contrast as well as 'inversion' of the feature, but the explanation is based only on the variations occurring within the reststrahlen range. The additional variation of emittance with particle size in the neighbourhood of the feature (cf. Figure 3; variation of emittance at ~ 8 and $\sim 10.5 \mu\text{m}$) has not been taken into account. Salisbury and Easters (1985), on the other hand, pointed out that rather porosity is the principal variable involved in loss of spectral contrast. But the increased porosity alone, occurring for decreasing particle size, can hardly explain the formation of inversion bands.

Additionally, the emission spectrum of a particulate sample is influenced by the sample's thermal conductivity. For the experiments of this work, however, the mean free path of the gas atoms (about $0.06 \mu\text{m}$) is considerably below the size of the particles and pores. Therefore, any change of thermal conductivity as a function of particle size is neglected (Jakosky, 1986).

5. Conclusion

The appearance of mid-infrared spectra of particulate minerals varies considerably in dependence on particle size. The observed well-known variation of various spectral features with particle size can be interpreted in terms of the photon's mean free path which follows opposite trends in the wavelength regions characterized by normal and anomalous dispersion, respectively.

The for decreasing particle size usually observed loss in spectral contrast results from opposite dependencies on the photon's mean free path L in the normal and anomalous dispersion wavelength regions. A decrease of particle size usually tends to equalize the values of L within and outside of the reststrahlen range.

The for decreasing particle size sometimes observed increase of spectral contrast – i.e. the formation of emission maxima in the reststrahlen range – occurs if the opposite trends result in a higher value of L in the reststrahlen range than in the neighbourhood of the feature.

The full-contrast minima of emittance (reststrahlen features) can be used for mineral identification in coarse-grained samples. They appear if the particle size markedly exceeds the wavelength of radiation.

For mineral identification in fine-grained samples (comprising particles comparable or smaller than the wavelength of radiation) the emission maxima – i.e. Christiansen features as well as inverted reststrahlen modes – become important instead of vanishing or low-contrast emission minima.

The emission spectrum of a mixture comprising equal parts of fine and coarse-grained material shows the characteristic features of both grain size ranges. This suggests that the chance for mineral identification is not essentially restricted by the presence of fine-grained particles, although the spectrum is more complicated due to the simultaneous appearance of the different features of both grain size ranges.

Evidently, a sufficient radiometric sensitivity of the used spectrometer is required in order to utilize the whole information content of the emission spectrum. For composition analysis of planetary regolith the spectrometer should be able to resolve a spectral contrast of about 0.01. Suitable equipments available for the future then should allow efficient mid-infrared mineral identification also for the fines of planetary regolith.

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