Spectral Emittance and Reflectance of Powders

J. R. Aronson, A. G. Emslie, T. P. Rooney, I. Coleman, and G. Horlick

The emittance of well-sized corundum powders in the range between 1–30 μ has been measured by ir interferometry in the 7.5–25 μ region of the spectrum (400–1300 cm⁻¹). The spectral features persist for all particle sizes with some interesting relative intensity variations. The temperature of the radiating surface is determined by setting the emittance equal to unity at 1035 cm⁻¹. At this point it is known that both orientations of corundum have a refractive index close to unity and the absorption coefficient is quite small. Thus both the volume and the surface reflectance terms are negligible and hence the emittance is approx. 1. The same powders have been measured in reflectance using a Cary–White spectrometer. A quantitative comparison is made between the two techniques and Kirchhoff's law is shown to apply experimentally.

I. Introduction

In the course of a research program directed toward the development of a comprehensive theory of the spectral reflectance or emittance of natural surfaces, we are attempting to extend a theory previously proposed by some of us[1,2] into the difficult region where the radiation wavelength approaches the particle size of particulate media. To aid in the formulation of this theory, we have made ir measurements on a series of well-sized corundum powders. This paper reports the experimental results. Corundum was chosen for this experiment as it satisfied several requirements necessary to shed light on the fundamental phenomena involved. The requirements include well known values of the optical constants for different particle orientations, and availability in well known and relatively narrow particle size distributions encompassing those wavelengths that contain the most interesting spectral properties for remote sensing purposes, which lie in the vibrational region of the ir. The choice of an interferometer for measurement of emittance spectra was suggested by its rapid response and high sensitivity for viewing extended sources.[3] This would be particularly important when short observation times are required as in remote sensing applications.

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II. Experimental

The experimental samples were Microgrit WCA aluminum oxide precision lapping powders manufactured by Microabrasives Corporation of Westfield, Massachusetts. This material was confirmed to be α-Al₂O₃ by x-ray diffraction. The manufacturer states[4] that each particle is a discrete crystal and has a purity of over 99%. The crystals have a platelet shape with their thickness averaging about one-fifth of their diameter. The c axis is perpendicular to the platelet face. Figure 1 shows the particle size distribution of the materials[4] and Fig. 2 is a stereo pair of photomicrographs of the surface of one of the samples as used in our experiment. The photomicrographs were obtained using a secondary electron image made with a JSM-2 scanning electron Microscope, courtesy of G. Coggswell, Dr. J. Russ, and A. Kabaya of JEOLCO, U.S.A., Incorporated. The samples were prepared by pouring the powders into 1-cm diam aluminum cups and smoothing with the edge of a spatula. Following evacuation of the air, the process was repeated several times in order to fill the cups. The surfaces were then shadowed using a Pd 40%:Au 60% alloy and photomicrographs obtained of the central areas in order to reduce edge effects.

The excellent depth of focus of these photographs clearly shows the complex nature of the powder geometry with which any theory must cope. In particular, the contrast between regions of particle agglomeration and deep cavities is very marked. The highly nonspherical shape of the particles is also evident and must be borne in mind in formulating a theory of the reflectance spectra of such samples.

The instrument used was a Block model 195TC interferometer spectrometer[5] which has a nominal spectral range of 4–40 μ and a spectral resolution of about 15 cm⁻¹. The interferogram was scanned repetitively at a rate of 1 spectrum/second for 2 min and the data
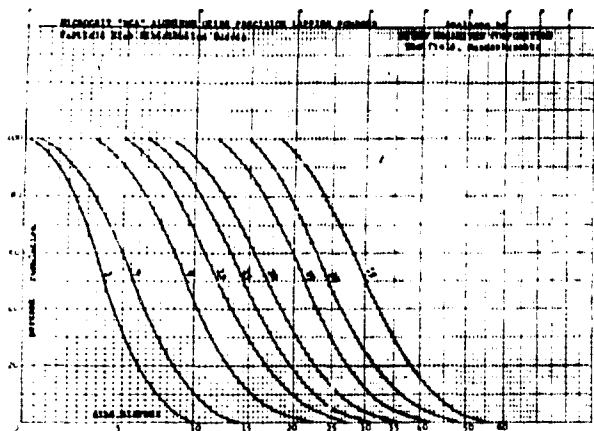
Fig. 1. Particle size distribution curves.

recorded on a Sony tape recorder for later reduction. The detector temperature was maintained at 305.5 K while the sample temperature as measured by a thermistor buried just under the surface was in the range between 294 K and 302 K for all samples.

The samples were placed in a flat aluminum pan in a hot plate maintained at 340.4 ± 0.6 K. The internal depth of the pan is 0.858 cm; this enables the optical properties of these powders to prevent any radiation from the pan itself reaching the interferometer. The entire assembly was placed in a sample chamber consisting of a black box constructed from 3.18-mm copper plate and insulated with a 5-cm layer of Styrofoam.[6] This chamber was flushed with nitrogen and cooled to approximately 207 K by filling a compartment of the chamber with dry ice. The cooling is necessary as a temperature differential between the sample and its surroundings and is required in order that sample reflection of ambient radiation does not precisely mask the self-emission of the sample. Cooling of the background was chosen in preference to the more usual practice of heating of the sample in order to more closely simulate the properties of real surfaces in remote sensing applications.

Experimental runs were made on WCA Al_2O_3 powders 5, 9, 15, 20, and 30 (which represent the nominal particle sizes, i.e., the platelet diameters, in microns). Each sample was poured into the sample pan, which has a diameter of 9.85 cm designed to fill the field of view of the interferometer. The top surface was leveled by passing the edge of a spatula across it. This worked well for the larger sizes but the 5 μ sample invariably had a roughened surface as agglomeration of the particles resulted in some gouging during the leveling procedure. The volume fractions were measured for each of the samples and were WCA 5 ($f = 0.286$), WCA 9 ($f = 0.287$), WCA 15 ($f = 0.290$), WCA 20 ($f = 0.319$), and WCA 30 ($f = 0.339$). This trend confirms our previous assertion that fine particles tend to pack loosely.[2] The interferometer scans were made at an emission angle of 45° with a 10° angle of view. The

measured data from the individual scans were coherently added and then the Fourier analysis was carried out to obtain the spectrum.

To obtain the absolute measurement of emittance, the instrument was calibrated by making measurements of a conical blackbody source at a number of temperatures which bracketed the range of intended sample temperatures. The detector was maintained at 305.5 K as in the sample measurements. The object of this calibration was the determination of the spectral responsivity of the instrument. The responsivity is the ratio of output signal units of the Fourier transform to the differential radiance between the detector and the source. A byproduct of this procedure was a radiometric confirmation of the detector temperature.

For reduction of the experimental corundum data, the output signal was divided by the responsivity to determine the differential radiance for each sample. The sample radiance was then determined by an additive correction for the known detector and sample chamber radiances. The determined radiances show slight systematic errors caused by small anomalies in the responsivity data. These include the residual effect of atmospheric absorption which was largely excluded during sample runs by flushing with nitrogen.

III. Surface Temperature

While our radiance plots were adequately calibrated, an appropriate blackbody temperature is necessary in order to plot spectral emittance accurately. As the thermistor bead was placed just under the surface of each sample, small variations in position would allow some discrepancy between the measured temperatures and those sensed by the interferometer. In addition, the spectral variations in optical properties of the powder would lead to some variation in the depth at which the radiation originates and, hence, to a variation in appropriate blackbody temperature due to the thermal gradient that exists. The optical constants for corundum are such that the radiation is emitted from depths ranging between a few microns and a millimeter in this spectral range. The temperature gradient over this

Fig. 2. Corundum powder surface (15 WCA) stereo pair made with JSM-2 scanning electron microscope (1500×).

Fig. 3. Emittance spectra of corundum powders.

depth is of the order of 5°C/mm. Therefore, even the physical size of the bead would lead to higher measured temperatures than those truly representative of the real surface. In order to obtain an accurate surface temperature for purposes of intercomparison of these spectra, we might have tried more precise experimental techniques. Instead, however, we chose a theoretical approach to this problem.

An examination of the lattice vibration spectra published by Barker[7] suggested an interesting way of establishing the surface temperature. Both orientations of corundum are seen to undergo zero Fresnel reflectance at a wavelength of just less than 10 μ. This is caused by the drop in refractive index (anomalous dispersion) that occurs at wavelengths just prior to strong absorption features. The index in this region falls below a value of 1. When the refractive index equals 1, the normal incidence Fresnel equation has the form

$$R = k^2/(4 + k^2), \qquad (1$$

where k is the absorption index. If k is small at this point, the surface reflectance is effectively zero. Using Barker's data, we have computed the optical constants and established the value of k at this point to be between 1.5×10^{-2} and 4×10^{-2} for both orientations of corundum. Scattering also disappears due to the index value near unity leading to a volume reflectance[1] near zero, and so we decided to assume an overall reflectance of zero at this point. Thus an emittance value of unity was obtained from Kirchhoff's law for this spectral point which did represent the highest emittance value shown in our spectra. By using this criterion ($\epsilon = 1$ at 1035 cm^{-1}), we were able to establish a blackbody temperature representative of the surfaces. These temperatures were used to compute the emittance curves shown in Fig. 3. The temperatures are somewhat lower than those measured at the location of the thermistor, which is in accord with the opacity of corundum. Further, the trend of the temperatures clearly shows the largest gradient occurs with the smallest particle sizes and greatest porosities.

IV. Results and Discussion

Figure 3 shows the resulting emittance plots for the five samples of corundum powder. The spectra fall into a systematic series for the most part, although some crossings of the curves occur near 400 cm^{-1} and 500 cm^{-1}. This emittance trend which has been observed by others,[8,9] might be explained in terms of the surface structure of the samples. The porosities trend such that the smaller particle samples have the greater porosities. The optical constants of corundum in much of this spectral range (400–900 cm^{-1}) are such as to give moderately high surface reflectance and, except for the smallest particle sizes involved, there is considerable absorption before reaching a second interface. Thus, any surface roughness leading to multiple reflection of a given incident ray would appear to be able to diminish over-all reflectance by multiple bounce and hence increase emittance. The trend we see with particle size could therefore be explained by assuming that the more porous sample has a greater amount of surface cavities and greater surface roughness (which was observed during the experiment). The data we obtained above approx 1300 cm^{-1} show the presence of intense atmospheric water bands and have been eliminated
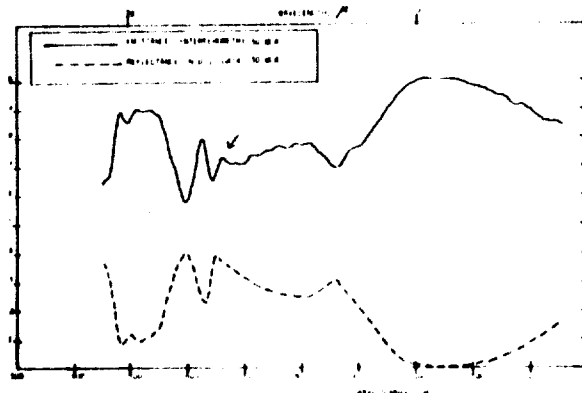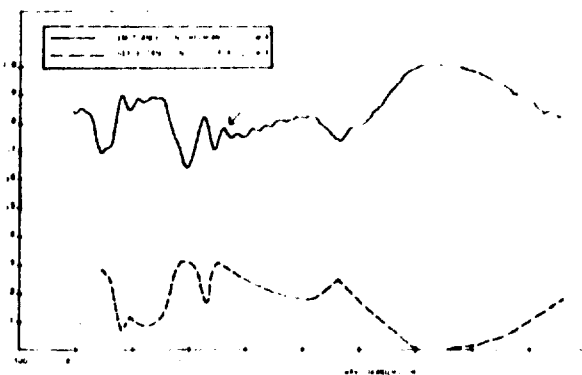

Fig. 4. Spectra of corundum powder.

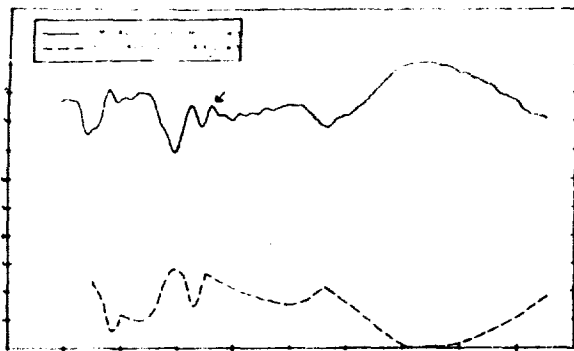Fig. 5. Spectra of corundum powder.
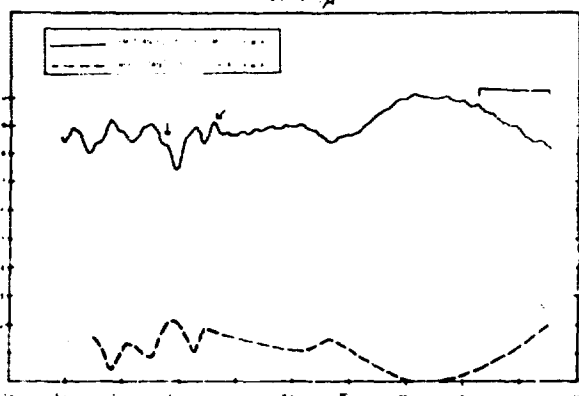
Fig. 6. Spectra of corundum powder.

Fig. 7. Spectra of corundum powder.

from our figures. There is some deviation from the observed trend of higher emittance from smaller particle sizes at frequencies beyond 1100 cm⁻¹.

In Fig. 4–8 we show the emittance data for these samples together with reflectance data for the same samples obtained at the National Bureau of Standards.[10] The reflectance data was obtained by a Cary-White model 90 recording spectrophotometer having approx 10-cm⁻¹ resolution. The samples were irradiated hemispherically and reflectance was measured at a 20° angle of reflection with an angle of view of 12° × 14°* in comparison to the 12° cone for the Block interferometer. The temperature of the samples was reported to be kept at 25°C. This direct comparison of emittance and reflectance measurements shows that Kirchhoff's law is quantitatively consistent with the data. It should be recalled that the temperature of the emitting surface was chosen by invoking Kirchhoff's law at a single frequency (1035 cm⁻¹). This temperature was then used to establish the emittance at all

* Private communication from John U. White 80 Lincoln Ave., Stamford Connecticut.

the other frequencies of the experiment. The agreement between these emittances and the independently determined values of (1-reflectance) over this wide frequency range is, therefore, a quantitative validation of Kirchhoff's law. The good agreement also confirms the validity of this method of the determination of surface temperature.

It is important to recognize that Kirchhoff's law,

$$\epsilon = 1 - R, \qquad (2)$$

applies only to the proper angular complements. The only qualifications necessary in our case are the use of 45° emittance data and 20° reflectance data which is not expected to be serious and the effects of the differing temperature gradients which can only be important for the emittance data as the optical constants are not significantly affected by the small temperature range involved. These factors may account for small shape differences between the emittance and reflectance data. It is to be noted that the measured reflectance values of zero near 1035 cm⁻¹ verify our theoretical method of establishing the reflectance at this point.

We observe some additional structure in emittance when compared with the shape of the comparable reflectance spectra. It is due in part to atmospheric bands in the calibration data resulting in apparent peaks in the spectra. For instance, there is an apparent emittance peak near 660 cm⁻¹ due to carbon dioxide (indicated in the figures) and there are peaks appearing both at the high-frequency end of our range and near 575 cm⁻¹ due to water vapor.

It is apparent from the data that the spectra of the larger particles have the greatest spectral excursions as has been observed by many workers. But even at the smallest particle sizes studied, there is ample signal-to-noise in the spectrum to clearly show the peaks and valleys that contain the compositional information. Comparison of the data from runs on the various particle sizes shows shape changes that need to be well understood before one could definitely identify a complex material by its spectrum. This is well exemplified by
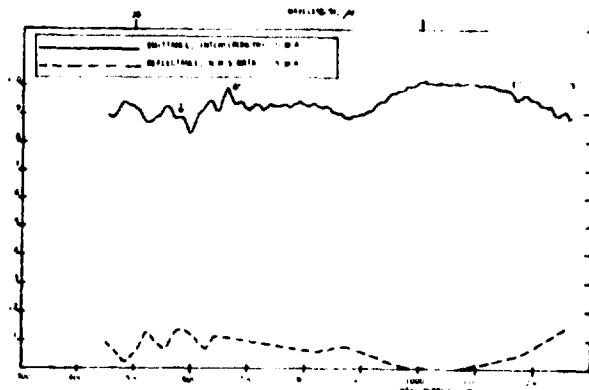
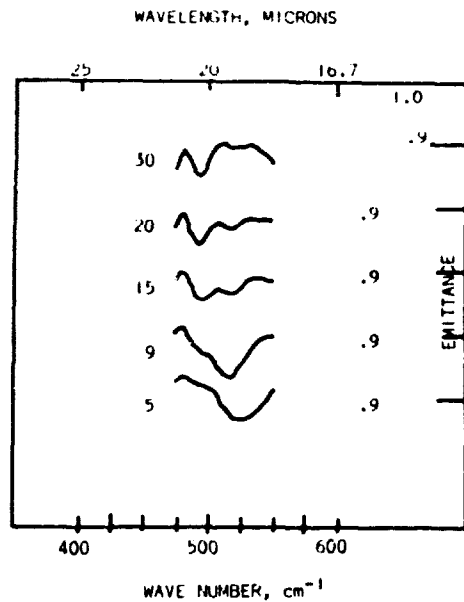

Fig. 8. Spectra of corundum powder.

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Fig. 9. Emittance features near 500 cm⁻¹ (displaced format).

Fig. 9, where the data from Fig. 3 in the vicinity of 500 cm⁻¹ is replotted in a displaced form so that the band changes can be clearly seen. There are different trends in the intensities of the two minimum emittance bands at 492 cm⁻¹ and 518 cm⁻¹ as a function of particle size. The band at 518 cm⁻¹ falls in intensity as the particle size is increased while the trend with the 492-cm⁻¹ band is in the opposite sense, although the three larger particle sizes appear to produce no change in band intensity. However, in general it may be said that in these experiments, features are preserved from spectrum to spectrum with some changes in intensity ratios and some minor frequency shifts.

As has been pointed out in the past,[1,2,11,12] grosser spectral changes with particle size can also occur. These depend on a number of factors including the particle opacity, topography, and the ratio of particle size to radiation wavelength. These factors influence both the surface and volume contributions to the reflectance in complicated ways.

We are currently in the process of computer modeling our theory of reflectance (emittance) from particulate media in the expectation that this type of approach will enable faster progress to be made in understanding the complicated processes involved in interpreting spectra such as those shown in this paper. In the course of this work, we discovered a minor error in our previous computer calculations of the theoretical spectrum of quartz.[2] We had used volume fraction ratios of 2:1 for $E\|C{:}E\perp C$ quartz crystallites in attempting to simulate quartz powder spectra rather than 1:2 as is correct for unpolarized radiation. We therefore reran the computations and found a much better match to the intensity ratios of peaks in the 500 cm⁻¹ to 300 cm⁻¹ measured in our previous work.[2] However, the peak intensities still differ from the experimental values.

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13. ABSTRACT

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