

EXPERIMENTAL VERIFICATION OF VALIDITY FOR KIRCHHOFF'S LAW ($E=1-R$) IN VACUUM AND PURGED AIR. A. Maturilli¹, J. Helbert¹, M. D'Amore¹, S. Ferrari¹, ¹Institute for Planetary Research, German Aerospace Center DLR, Rutherfordstr. 2, 12489 Berlin, Germany – alessandro.maturilli@dlr.de

Introduction: The simplest postulation (without wavelength or directional subscripts) for Kirchhoff's law reads $\mathcal{E}=1-R$, where \mathcal{E} is emissivity and R is reflectance. However, Kirchhoff's law was originally postulated for opaque materials in thermodynamic equilibrium with the surrounding medium (meaning the sample is isothermal and at the same temperature of the background to which it radiates) [1]. Such a condition is rarely found in laboratory on Earth and never met in space; nevertheless, for simplification or lacking of suitable emissivity datasets (and being reflectance measurements much easier than emissivity measurements), Kirchhoff's law is widely used to substitute emissivity with 1 minus reflectance measurements (and often bi-conical or bi-directional reflectance is used, and not hemispherical as it should be).

The purpose of this paper is to show the behavior of emissivity vs. bi-directional reflectance measurements for samples of small to large grain sizes, under vacuum or purged air, at various sample temperatures.

Experiment description: At the Planetary Emissivity Laboratory (PEL) of the German Aerospace Center (DLR) we measure emissivity, reflectance, and transmittance of materials from the visible to far infrared spectral range. For the experiment reported in this paper we used a Bruker Vertex 80V Fourier Transform Infrared-Spectrometer (FTIR), operated under vacuum or under purging condition to remove atmospheric features from the spectra. An external evacuable chamber is used to measure emissivity. Induction heating system allows to heat up the samples (in stainless steel cups) from 50°C to higher than 800°C. Bruker A513 accessory is used to obtain bi-directional reflectance with variable incidence angle i and emission angle e between 13° and 85° at room temperature. For this experiment, we kept the i and e angles to their minimum of 13°.

This comparison study involved samples of small grain sizes (<25 μm) and large grain size (125-250 μm) measured under vacuum ($P<0.8$ mbar) and purged air environment, at various temperature steps. Those temperature steps were determined by giving fixed current values to the induction heating system, resulting in 260°C, 350°C, and 415°C in vacuum and 200°C, 290°C, and 375°C under purging. We measured spectra of 5 samples (quartz, ilmenite, diopside, pyrope, and labradorite); in this paper we show only results for quartz. Each cup containing one of the samples was measured in vacuum, then cooled down, and measured again heated under purging without changing the sam-

ple, to avoid any experimental error. All spectra are shown without smoothing or any other artifact.

Emissivity vs reflectance: Figure 1 shows emissivity for quartz <25 μm sample in purged air, measured at 3 temperatures. The emissivity spectra of quartz at increasing temperatures look identical within 1% error, as we already showed in [2] and [3]. To note the water lines between 5 and 8 micron, and small CO_2 features at 4.3 and 15 micron.

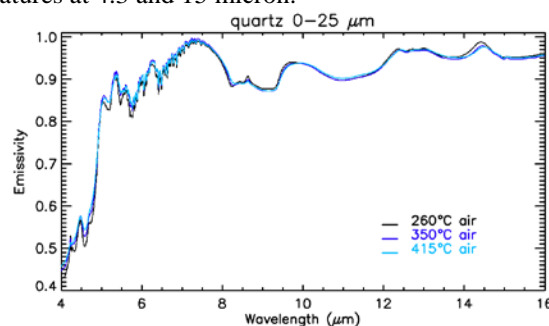


Figure 1. Quartz <25 μm emissivity in purged air.

In Figure 2, emissivity of the same quartz sample measured under vacuum is shown.

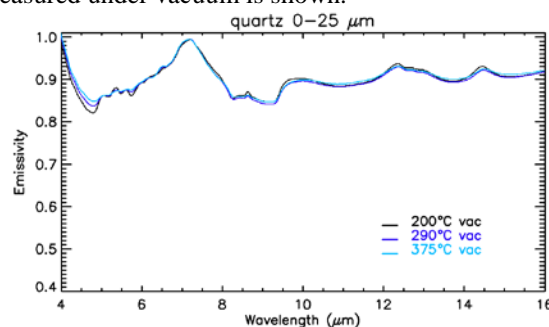


Figure 2. Quartz <25 μm emissivity in vacuum.

Emissivity spectra in vacuum and purged air do not differ significantly in the Reststrahlen band region; however in the region above 12 μm the continuum for the vacuum spectra is about 5% lower than for purged measurements. Emissivity maximum or Christiansen Feature (CF) shift from 7.35 μm for purged spectra to 7.2 μm for vacuum, and the shape of region around the CF shows important changes, narrowing for the case of vacuum data (well known effects of thermal gradients in the sample under vacuum [1]). Below 6 micron the continuum looks very different for the 2 cases, although all the minor water bands between 7 and 5 micron can be still identified. This is mainly due to increasing transparency of quartz (occurring only under

vacuum !!) added to increasing emissivity of stainless steel cups: we look through the sample to a hotter steel cup, this determine the emissivity increase for wavelengths shorter than 5 micron.

1-reflectance spectra of the same quartz <25 μm sample in purging and vacuum shows no difference (Fig. 3). Although this curve resembles much the one for emissivity in purging, some important variations are found. The shape of the region around minimum in reflectance (also maximum in 1-R) differs, so like the curve behavior below 5 micron: an effect of multiple surface scattering increasing with reduction of grain size [4].

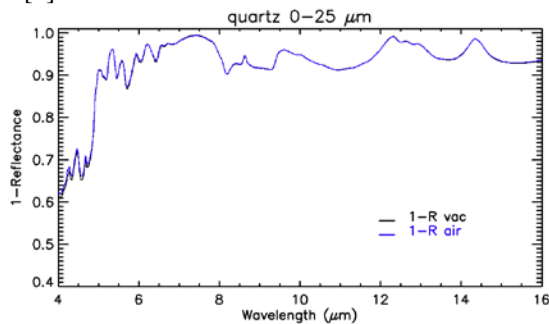


Figure 3. Quartz <25 μm 1-reflectance in purging and vacuum.

In Figures 4, 5, and 6 we show the same kind of measurements for a quartz 125-250 μm sample.

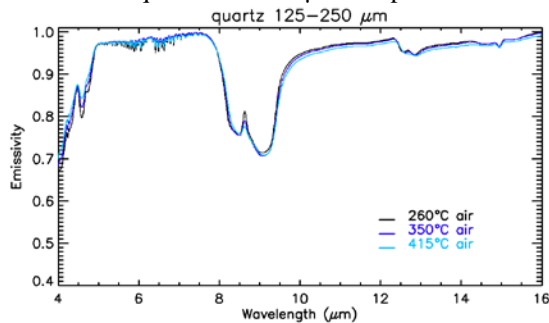


Figure 4. Quartz 125-250 μm emissivity in purged air.

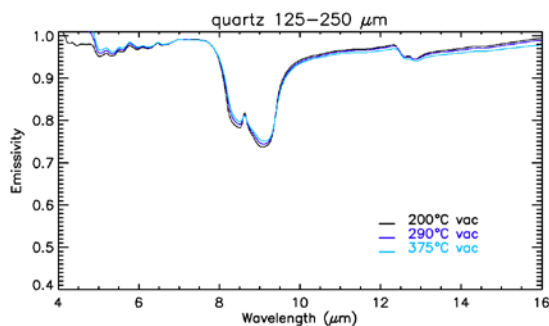


Figure 5. Quartz 125-250 μm emissivity in vacuum.

The spectra look very similar in the region above 5 micron. Reststrahlen region is around 5% deeper for the data taken under purging. No modification in the region around the CF is noticed. Below 5 μm we see the same effect of increasing emissivity for the measurements under vacuum that we described for the fine grain size. In Figure 6 we can see how identical the 1-reflectance curves are for the samples under purging or vacuum. For this larger grain size multiple scattering effects are much reduced, so we do not notice extended changes in the spectral region below 5 micron.

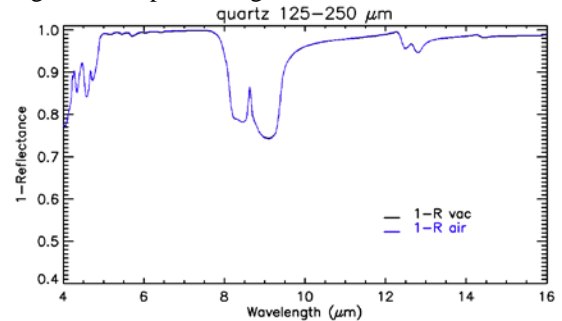


Figure 6. Quartz 125-250 μm 1-reflectance in purging and vacuum.

Conclusion and outlook: At the Planetary Emissivity Laboratory (PEL) of DLR we measured reflectance (at room temperature) and emissivity from approx. 200°C to 400°C of the same sample under vacuum and then under purged air, without moving the sample, to experimentally study the validity of Kirchhoff's law $\epsilon=1-R$. Five minerals have been chosen for this comparison, for each of them we measured fine (<25 μm) and large (125-250 μm) separates. For a quartz sample (shown in this paper), we found differences between emissivity under vacuum, under purging and 1-R (R is bi-directional reflectance), whose intensity is strongly affected from particle size range, being stronger for fines and much more limited for larger particles. 1-R show no variations from vacuum to a purged environment. The work presented here is to be completed with emissivity measurements at approx. 100°C (resembling Moon and asteroid surface temperature) for all the samples, and only for quartz, a measure at $T>600^\circ\text{C}$ to detect spectral variations for the transition from α -quartz to β -quartz.

References: [1] Salisbury J. W. et al. (1994) *JGR*, 99, 11897–11911. [2] Helbert J. and Maturilli A. (2009) *EPSL*, 285, 347–354. [3] Maturilli A. and Helbert J. (2014) *JARS*, 8, 1–12. [4] Salisbury J. W. et al. (1994) *JGR*, 99, 24235–24240.