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Size-dependent laser-induced heating of solid particles studied by Raman micro-spectroscopy

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Significant laser-induced heating has been observed for micron-sized solid particles by Raman micro-spectroscopy. At laser power densities relevant for operation of the Raman Laser Spectrometer instrument on board of the future ESA's ExoMars 2018 mission, a local temperature increases already for the silicon particles with the median sizes below 250 μm . Complex olivine minerals express significantly lower laser-induced heating than those for silicon grains.

Small solid particles including also submicron-sized ones (often called as dust) are typical samples returned by probe space missions to solar system bodies (the moon, asteroids) and from interplanetary medium as well as found on the Earth surface as micro-meteorites. Chemical analysis of this material gives a key knowledge on the formation and evolution of stars and planetary systems.

As a non-destructive technique, Raman spectroscopy comes to the front of in situ (future ESA ExoMars mission) and laboratory analysis (meteorites as well as dust from the sample return space missions: Apollo, Luna-24, Stardust, Hayabusa) with a potential for a direct search for organic/biological matter without necessary sample preparation, requiring only optical access to an investigated sample. On the ExoMars rover the sampled rock (diameter of ~ 11 mm, length up to 35 mm) will be crushed to powder with a median grain size of 250 μm and with 90% falling between 50 and 500 μm , that would satisfy requirements of all instruments in the rover scientific payload [1]. Since each investigated sample is shared for different instruments, there are specific requirements for a temperature range that would allow to protect volatiles trapped in the rock sample and to avoid possible temperature catalyzed processes.

Since inelastic scattering of light is a relatively weak process, especially for complex rock materials, significant laser power densities (up to 10 $\text{mW}/\mu\text{m}^2$) are often required for a detectable Raman scattered light. The deposited power has to be scattered into the particle, but heat dissipation efficiency losses for particle sizes

approaching mean free path of characteristic thermal phonons. As a result, a local hot spot and significant heating of a whole particle can be induced under required for Raman spectroscopy laser intensities. Local temperature of a particle can be derived from the Raman frequency, the Raman linewidth, and the ratio of the intensities of the Stokes (S-) and anti-Stokes (AS-) signals [2-5].

Silicon, having a large Raman scattering efficiency and a clear optical phonon line, has been thoroughly studied by Raman spectroscopy under conventional heating of bulk crystals [2,3] as well as under laser-induced heating of nanoparticles (< 100 nm) [4,5]. The latter indicate on significant local heating reflected in the increased AS/S intensity ratio, decreasing relative S-, AS- frequencies and a phonon line broadening.

We focused on particles of crystalline silicon (as a reference material) and olivine minerals (as an important rock-forming silicate and one of the most abundant phase in the solar system, including the Earth's upper mantle) with mean sizes of grains from 25 μm to bulks. The bulk solids were consequently crushed and sifted into sets of particles with median sizes of 25-45-63-90-125-180-212-250-355-500 μm . Raman spectra were taken from a single standing particle without a contact to neighbors to ensure minimal thermal conductive link, including one into the glass holder plate. The Raman measurements were performed with a Witec Alpha 300 Raman confocal microscope. The excitation laser wavelength is 532 nm; the spectral resolution is about 4 cm^{-1} . With a 100 \times objective the $1/e^2$ spot size on a sample is less than 1.5 μm . Each measurement had

the acquisition time of 120 s. The power on the sample was varied step-like between 50 μ W and 13 mW. Raman spectra were taken in the range of relative $0 \pm 2000/\text{cm}$ for Stokes and anti-Stokes bands. The S-, AS-bands within $0 \pm 200/\text{cm}$ were not accessed due to the used notch filter.

Silicon particles: Silicon Raman spectrum has an expressed LTO phonon line at the Brillouin zone center at about 520/cm (room temperature, natural isotopic content, bulk crystal) with lower intense peaks at some sum phonon frequencies. Analysis of temperatures derived from the AS/S intensities ratios indicate on temperature related effect for silicon particle of sizes under 250 μm . Largest derived temperature rise has been observed for the smallest, $\sim 25 \mu\text{m}$ particles, up to 1000 K if calibrated to the references [2,3]. This, however, does not coincide with the values derived using the reference data on the LTO phonon line shift or linewidth in bulk silicon [2,3]. We also observe nonlinear slope of temperature gradient with a laser power, differently to those reported in [5]. Additional strong phonon mode occurs spectrally resolved on the red side of the LTO mode for the particles with mean sizes below 150-200 μm and rises up with laser power up to the intensity of the LTO phonon line. The same line has been reported earlier in the Raman spectra of 5-10 nm particles [4] and was attributed there, together with the LTO mode, to surface phonon modes in silicon nanoparticle.

Olivine particles: Olivine minerals (general chemical formula $[\text{Mg}_{2-x}\text{Fe}_x]\text{SiO}_4$) have two characteristic phonon bands: in high frequencies, from $\sim 800/\text{cm}$ to $\sim 1000/\text{cm}$ (internal SiO_4 tetrahedra stretching modes) and low energy lattice modes of mixed $[\text{Mg}_{2-x}\text{Fe}_x]$ cation translations, 0-600/cm, and external SiO_4 vibration modes, $\sim 400/\text{cm}$ [6]. Temperature related measurements on bulk olivine with different cation compositions [6,7], recorded in Stokes band, show mostly intensity changes in the SiO_4 stretched modes, while low-frequency bands shift and undergo line-broadening. No reference data on AS/S intensity ratio dependent on local temperature has been reported, to

our knowledge, on phonon modes in olivine. Since AS- and S-intensities suffer from diffuse scattering on small grains, their Raman spectra deliver only weak features from the most intense lines, that are the lines at $\sim \pm 820-860/\text{cm}$ in high frequency band. In contrast to silicon particles, we did not observe detectable regular modification of line intensities, line positions in the high-frequency band Raman spectra of olivine at energy power density specified for the ExoMars rover lab [8] for all grain sizes. Slight rise up of the AS/S intensity ratio has been detected for the most small particles and highest laser powers.

The estimates on heating of olivine particles with a mean size of $\sim 50 \mu\text{m}$ show that the temperature rise does not exceed 100 K for the laser power densities aimed for the RLS instrument on the ExoMars rover, that is acceptable for the "nondestructive" mode of the sample handling in the rover scientific lab.

References

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