Contents lists available at ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

Laser-induced alteration of Raman spectra for micron-sized solid particles

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A R T I C L E I N F O

A B S T R A C T

The Raman Laser Spectrometer (RLS) instrument on board of the future ESAs ExoMars mission will analyze micron-sized powder samples in a low pressure atmosphere. Such micron-sized polycrystalline solid particles might be heated by the laser during the Raman measurements. Here, we report on the temperature-induced alteration of Raman spectra from micron-sized polycrystalline solid particles by comparing Raman spectra on silicon and the rock forming minerals olivine and pyroxene taken at different laser intensities and different ambient temperatures. Our analyses indicate that laser-induced heating results in both broadening and shifting of characteristic Raman lines in the Stokes and anti-Stokes spectral regions. For elementary crystalline silicon a significant local temperature increase and relevant changes in Raman spectra have been observed in particles with median sizes below 250 μm. In comparison, significantly weaker laser-induced Raman spectral changes were observed in more complex rock-forming silicate minerals; even for lower grain sizes. Laser power densities realized in the RLS ExoMars instrument should cause only low local heating effects and, thus, negligible frequency shifts of the major Raman lines in common silicate minerals such as olivine and pyroxene.

1. Introduction

Small particles including submicron-sized ones (often called dust) are typical samples from sample return space missions to solar system bodies (e.g. the Moon and asteroids) or to the interplanetary medium. On Earth small extraterrestrial particles are recovered as micrometeorites. The chemical and physical properties of this material give key information on the formation and evolution of our solar system. Non-destructive and non-invasive techniques such as Raman spectroscopy comes to the front of in situ (e.g., the future ESA Exo-Mars mission (Rull et al., 2013)) and laboratory analysis (meteorites as well as dust from the sample missions: Apollo, Luna-24, Stardust, Hayabusa (Böttger et al., 2014)). For Raman spectroscopic investigations it is sufficient to have optical access to the investigated object. In addition to analyzing the chemical and structural properties of inorganic minerals, Raman spectroscopy allows to identify and, thus, search for organic/biological matter. No sample preparation is necessary.

For the ExoMars rover lab it is planned to collect Martian surface samples (~11 mm diameter cores up to 35 mm in length). These cores will be crushed to powder with a median grain size of 200–250 μm and with 90% falling between 50 and 500 μm (Rull et al., 2013). Such a grain size distribution would satisfy the requirements of all instruments

of the rovers' scientific payload (Bost et al., 2015). Because each sample will be successively analyzed by different instruments it is important to know about possible modifications of the samples due to previously applied analytics. It is, for example, important to know if the Raman measurements would heat micron-sized grains to temperatures at which specific volatiles are mobilized or possible temperature catalyzed processes are initiated. We therefore compare Raman spectra from mineral grains of different sizes heated to a given temperature.

Since inelastic scattering of light is a relatively weak process (typical scattering efficiency below 10^{-7}), the spectral detection of the inelastic scattered light requires significant laser intensities. A light power density on a sample surface of up to $1.2\,kW/cm^2$ and a spatial resolution of about 50 μm will be provided by the continuous wave 531.5 nm laser in the Raman Laser Spectrometer (RLS) on the ExoMars rover (Rull et al., 2013). The power of the laser is scattered by different heat transfer mechanism(s) within the multimineral grain and between the individual grains in a powder. At environmental temperatures below 300 K (room temperature) the heat transfer in the grain is dominated by phonon-related interactions. Although being distinctly restricted to a single crystal, the properties of heat transfer in multimineral samples like rocks are still poorly understood. The theoretical predictions of heat dissipation quantities, such as the thermal diffusiv-

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ity of Earth-like upper mantle rocks, differ significantly (about 30% (Gibert et al., 2003)) from the measured values. Dense grain boundaries, micro-cracks and a variety of other defects hinder the phonon transport and, thus, reduce the thermal dissipation in the polycrystalline material. During Raman spectral measurements, the heat diffusion from a laser spot becomes inefficient for particle sizes approaching the mean free path of characteristic thermal phonons. Experimental studies reveal typical mean free paths in crystalline silicon spanning 0.3–8.0 μm at about room temperature (Johnson et al., 2012; Regner et al., 2013) while in more complex minerals such as olivine and pyroxene it does not exceed a few nanometers (Kobayashi, 1974). Additionally, between different grains in the powder the complex, highly irregular surface shape of the crushed powder or extraterrestrial particles prohibits an extensive thermal contact to the surrounding particles. The pore spaces would serve as an insolation because of a low atmospheric density on Mars or especially on the Moon and asteroids. As a result, local hot spots (Maris, 1986) and significant heating of a whole particle may be induced by laser intensities required for Raman spectroscopic investigations.

The influence of grain size on the recorded Raman spectra using a RLS prototype for the ExoMars mission 2018 was studied by Foucher et al. (2013). They focused their study on the feasibility to identify minerals in powdered samples using the fixed values of characteristic phonon lines in the Stokes Raman spectra collected with specific laser power densities and particle sizes. In rock samples with a mean powder particle size and a laser spot corresponding to those expected during the operation on a Martian rover these authors (Foucher et al., 2013) did not find detectable changes in the Raman spectra from a variety of different minerals. They however, reported significant changes in the Raman spectra using the same samples but a commercial Raman spectrometer with larger irradiation doses due to stronger focusing of the laser beam. The authors estimated that in some samples the local temperature increased up to 1000 K. These values are based on a classical formalism for the temperature determination using the ratio between the intensities of the Stokes (S) and the anti-Stokes (AS) components in the Raman spectrum.

However, corrections of this formalism due to a complexity of crystalline structures, laser absorption rates and particle sizes have not been taken into account. This omission may hide possible local temperature excursions in micron-sized particles that would result in either under- or overestimating the temperature increase in the bulk sample. To overcome this drawback, we here compare the laser-induced changes in the Raman spectra of powdered minerals across a broad range of laser irradiation rates with calibrated Raman spectra obtained from grains heated to a given temperature and measured with a fixed low level laser power. Since in the latter case the Raman spectral changes are independent from the laser irradiation, this calibrated data can be used to accurately determine the temperature in the samples, and thus the heating of the sample caused by the laser. This knowledge is critical in the complex analysis of particles because heating effects could lead to non-desired physical changes such as for example loss of volatiles or enhanced alteration of minerals.

2. Method

We determined the degree of heating by comparing the Raman spectral changes calibrated at different given temperatures with those changes observed by increasing the laser power. For this we used the different dependences of the intensities of the Stokes – and anti-Stokes lines upon temperature. So the intensity ratio of the Stokes to anti-Stokes Raman peaks can be used to evaluate heating effect of the laser irradiation.

Comparative analyses were conducted in different series of measurements. We systematically increased the laser power up to a laser excitation irradiance of 2.6 mW/μm², varied the particle sizes from a few mm down to a few μm and increased the temperature up to 800 K,
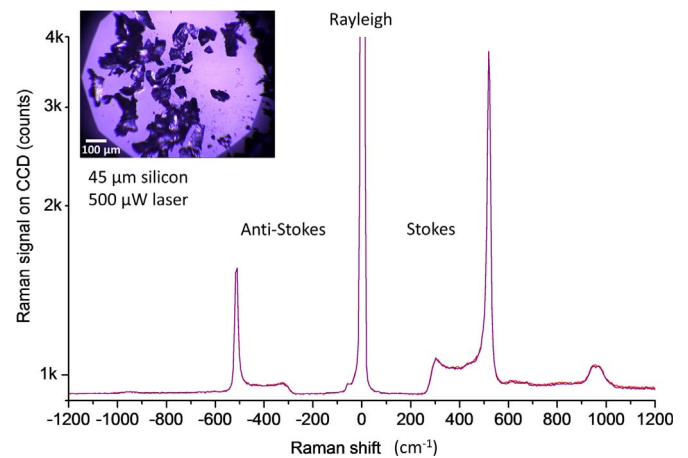

Fig. 1. Raman spectrum of a silicon particle of 45 μm size. The anti-Stokes and Stokes components of the scatterd light as well as the centered Rayleigh scattered laser line are shown. The signals in the ranges of $[-300\,cm^{-1}; +300\,cm^{-1}]$ are suppressed by the notch filter. The inset shows an image of typical silicon particles taken with the build-in camera.

while keeping the laser excitation power low at 500 μW. Here, we focused on the relative changes in the Stokes (S) and anti-Stokes (AS) parts of Raman spectra expressed as intensity ratios as well as frequency shifts of characteristic phonon lines.

Raman measurements were performed with a WITec Alpha 300 Raman confocal microscope. The excitation laser wavelength was 532 nm and the spectral resolution was about 4 cm⁻¹. Each measurement was collected with an acquisition time of 120 s. The power on the sample was varied in steps between 10 μW and 13 mW laser power translating to irradiances between (spot size is about 1.3 μm) about 2 μW/μm² to 2.6 mW/μm². The Raman spectra were taken in the range of relative 0 ± 2000 cm⁻¹ for the Stokes and anti-Stokes bands. The S- and AS-bands within 0 ± 300 cm⁻¹ were removed by the notch filter in use (Fig. 1). Equilibrium heating of the particles was realized with a Linkam TS1500 stage able to provide ambient temperatures of up to 1700 K. The investigated particles were placed on a ceramic holder of the evacuated stage, while the surrounding parts were cooled by a closed cycle refrigerator.

For the temperature dependent measurements the Raman spectra were collected both in the heating and cooling directions. After reaching the next temperature value, a special pause of about one minute was taken in order to ensure equilibrium temperature between the ceramic bath and the heated samples. The data obtained during the heating and cooling cycles differ slightly. The Raman spectra were analyzed for their spectral content, the linewidth and the position of characteristic phonon lines. These data have been obtained by fitting the spectral peaks with a Gaussian function. The accuracy of the determined peak position, peak magnitude and linewidth by the fits is better than 10^{-3}. The local temperature estimates were derived from the general expression for the ratio of the I_{AS} and I_S intensity components (Balkanski et al., 1983):

$$\frac{I_{AS}}{I_S} = F\left(\frac{\omega_L - \omega_S}{\omega_L + \omega_S}\right)^n \exp\left(-\frac{h\omega_S}{k_B T}\right) \qquad (1)$$

where F is the coefficient that depends on the absorption of pump and scattered light and the Raman cross sections for the involved frequencies, ω_L and ω_S are the pump and scattered frequencies, h is the Planck constant, k_B is the Boltzmann constant and T is the local temperature, $n \cong 4$ – as long as anharmonic contributions are not considered (Balkanski et al., 1983). Eq. (1) describes the ratio of I_{AS} and I_S intensities of scattered light reasonably well for different media assuming that local hot spots are not present. The absolute intensities in Stokes and anti-Stokes modes should be corrected by the spectral response of the used