Research article

Evaluation of portable Raman instruments with 532 and 785-nm excitation for identification of zeolites and beryllium containing silicates

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In this short paper we present Raman spectra of minerals of the group of zeolites and beryllium containing silicates (thomsonite, stilbite, natrolite, euclase, phenakite, bavenite, milarite and beryl) obtained indoors/outdoors on a collection of samples using a portable 532-nm/785-nm systems. This study complements a previous one in which one of the first handheld 785-nm excitation instruments was tested. To our knowledge this is the first time that a handheld Raman spectrometer equipped with a 532-nm laser as well as a portable dual instrument with 532/785-nm excitation was used in mineralogy. For the major findings of the zeolites investigated, the most intense Raman bands are found at correct positions $+/-2$–$4\,cm^{-1}$. Although acceptable results were obtained using the 532-nm excitations with both the instruments (the strongest bands are well developed and these bands permit the unambiguous identification), the use of the near-infrared excitation can especially be recommended (higher number of bands at correct positions, spectra with a S/N similar to laboratory spectrometers). Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: handheld Raman spectrometers; zeolites; beryllium-containing silicates

Introduction

Lightweight portable or handheld Raman spectrometers have become instruments that can be recommended for common geological fieldwork. As the miniaturization of these instruments has progressed, there are currently lightweight as well as palm-size Raman spectrometers that can nowadays be used for detection of unknown samples including minerals under outdoor conditions. For field geoscience measurements and applications as well as for areas as astrobiology Raman spectroscopy can be proposed as a technique of field detection and identification of minerals[1–5] and biomarkers.[6–11]

The approach of recording spectra of minerals for their mostly instantaneous unambiguous identification has been developed using especially the near-infrared diode excitation (785 nm).[3] Critical issues of outdoors work were highlighted recently including diverse analytical issues (collection of scattered light, time of accumulation).[3,4,12,13] Many black and dark minerals are not easy to identify using the portable systems because of absorption of the radiation and/or fluorescence emission. Positioning and focussing of the laser beam onto small grains can be a limiting factor in some cases.[4,13] However some of these observations are, at least at some level, common also when using lab based Raman microspectrometers and related with the properties of the compound. The potential use of the different miniaturized Raman systems available and their use in art, geoscience and forensic areas have been reviewed by Vandenabeele et al.[12] More recently, smaller and robust instruments have been developed, equipped also by less common 1064-nm or 532-nm excitation lasers. The 1064-nm system was evaluated for geoscience and forensic applications, confirming good performance.[7]

Zeolites are representatives of tektosilicates—they consist of periodic symmetric arrangements of corner-linked AlO_4 and SiO_4 tetrahedra combined generally with monovalent or divalent cations. Some of these phases can also by synthetized, and many interesting application features derive from their unusual structure. Silicates and

zeolites being common minerals of volcanic and other rocks were successfully investigated in detail since the seventies, and assignments of the Raman bands of common minerals have been carried-out.[14–20] The majority of previous papers on zeolites report data obtained using dispersive laboratory systems with Ar^+ lasers (514, 532 nm), and also a 488-nm excitation[15,18] or 633-nm source.[14] Our previous report showed that zeolites could be identified using portable Raman instrumentation equipped with a 785-nm diode.[19] There is a comparison between the performance of laboratory dispersive spectrometers, and near-infrared-excitation portable instrument is reported.

The main goal of the present work is to compare the new types of portable Raman spectrometers for zeolites. First, a new 532-nm laser handheld Raman spectrometer is evaluated; second, performance of a dual instrument—permitting measurements using alternatively both the excitations 785 and 532 nm—is tested. Critical technical aspects are highlighted to permit recommendations for future use of this type of instrumentation for zeolite detection.

Experimental

Samples

The same series of zeolites and Be-containing minerals specimens as those investigated previously in our group[3] was studied here. All of

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the mineral samples investigated in this study were kindly provided from the mineralogical collections of the Institute of Geochemistry, Mineralogy and Mineral Resources at the Faculty of Science, Charles University, Prague, Czech Republic. All the studied specimens are listed in Table 1 (along with their catalogue numbers plus any additional information, such as the locality). Table 1 reports details about the investigated samples. The collection specimens are broadly crystalline, crystal and aggregates dimension around 1–3 cm.

Raman spectra were recorded directly on the mineral specimens, without any previous treatment of the surface. Spectra were recorded indoors, few specimens outdoors as well under cloudy weather. No major difference was found between both the modes of collecting spectra.

Instrumentation

Three different portable Raman spectrometers were used in this work. Figure 1 presents the instruments and Table 2 their technical

Table 1. List of investigated minerals. All the specimens investigated originate from the mineralogical museum of the Faculty of Science (Charles University in Prague). Archive no. reported

Mineral	Formula	Origin	Collection
Thompsonite	$NaCa_2[Al_5Si_5O_{20}]\cdot 6H_2O$	Dobrna, Děčín CZ	45 321
Stilbite	$Ca\,NaCa_4[Al_8Si_{28}O_{72}]\cdot n(H_2O)$	Berufjordur, ICE	21 360
Natrolite	$Na_2[Al_2Si_3O_{10}]\cdot 2H_2O$	Lovozerska, RU	17 985
Euclase	$BeAl[OH|SiO_4]$	Sardagon, RU	18 024
Phenakite	Be_2SiO_4	San Miguel, BRA	5000
Bavenite	$Ca_4Be_2Al_2Si_9O_{26}(OH)_2$	Akudertia. Siberia RU	18 156
Milarite	$K_2Ca_4Al_2Be4Si_{24}O_{60}\cdot(H_2O)$	Giuv Tavetsch, CH	3295
Beryl	$Be_3Al_2Si_6O_{18}$	Prata, IT	Private collection

parameters. The first-one, Inspector Raman (Delta Nu), is a 785-nm system different from the first Defender (Ahura) which was applied in the previous investigation of zeolites and beryllium-containing minerals.[19] The second one is the lightweight 532-nm spectrometer (Rigaku), and finally the third one is the dual laser Raman spectrometer EZRAMAN-I-DUAL Raman system (Enwave Optronics).

The handheld Inspector Raman instrument (mass 1.9 kg) was manufactured by Delta Nu at Laramie, USA and equipped with a 785-nm diode laser for excitation with a maximum output power of 120 mW at source and a thermoelectrically cooled CCD detector with a wavenumber range of 200–2000 cm^{-1}. The instrument is also designed as a handheld pistol-like shape and is operated through the laptop connected via USB cable. The laptop computer is equipped with NuSpec software, which allows the control of experimental settings as well as saving the spectra. Laser power levels at source can be set to five settings: low, medium-low, medium, medium-high and high.

The FirstGuard (Rigaku) instrument weights 2.7 kg and is equipped with a 532-nm diode laser thermoelectrically cooled CCD detector. The maximum laser power output at source is 60 mW. It operates in the spectral range of 200–3000 cm^{-1} with the spectral resolution of 10–15 cm^{-1} as reported by manufacturer. It uses a resistive touch display and allows wider range of experimental settings. In this study the spectra were collected at the following settings: 10 accumulations for 1 s each and 1 accumulation 10 s long at the 50-mW laser power.

The portable dual laser Raman spectrometer allowing 532/785-nm excitation is described by Lauwers et al.[20] where it was tested for applications in the field of cultural heritage. This is an EZRAMAN-I-DUAL Raman system (Enwave Optronics, Irvine CA, USA). The fibre-optic-based spectrometer is equipped with a redion diode laser (785 nm) and a green Nd:YAG laser (532) with interchangeable lenses and adjustable power controller for each laser (maximum output power 400 mW and 100 mW for the 785-nm and the 532-nm lasers, respectively). A different grating is used in the spectrometer giving a different spectral range and spectral

Figure 1. Handheld instruments used in this study. Upper picture 532-nm excitation diode-equipped Raman spectrometer, lower picture 785-nm excitation diode-equipped Raman spectrometer and on the right dual system (532/785-nm excitation).

Table 2. Portable instruments used in this study

Type	Laser type (nm) power (mW)	Positioning	Control	Weight (kg)	Head	Power source	Spectral resolution (cm^{-1})	Manufacturer
Mobile								
EZRaman-I series	785, 532 400 (50)	Manual	Laptop	12	Optical fibre	Rechargeable Li-ion battery	6	Enwave Optronics Inc
Handheld								
Inspector Raman	785, (120)	Manual	Laptop	2.3	Fixed	Rechargeable Li-ion battery	8	Deltanu
First guard	532, (500)	Manual	Built-in computer display	2.3	Fixed	Rechargeable Li-ion battery	7–10	San Jose, USA—Rigaku

resolution for each laser. The spectrometer can use 230 V AC or an internal or external Li battery (Enwave Optronics), allowing for higher autonomy.

All instruments provide export of Raman spectra into the Galactic. spc format. Spectra were then worked with using GRAMS AI (Version 8.0, Thermo Electron Corp, Waltham, MA, USA). In some cases Raman spectra are baseline corrected, but no other spectral treatments were undertaken.

Typical data analysis times were 20–60 s, and multiple spectra were obtained for each compound; an optimization of the number of accumulations to improve the signal-to-noise ratio is automatically carried out by the software. The spectrometer automatically records a dark spectrum and subtracts this from the raw data to correct for signals internally caused by the spectrometer. Based on previous experience all outdoor measurements were carried out by careful shielding of the specimens and instrument measurement area using a black cloth. The identifications of minerals by portable instruments is based on comparisons of data with reference values reported in literature. For any problematic spectra (faint signals, fluorescence complications and bigger difference in wavenumbers obtained) and for better general future applications we collected spectra on the same specimens using a lab Raman microspectrometer. Obtaining at least half of the strong and medium intensity bands at correct positions $+/-3$ cm^{-1} was considered as sufficient for acceptable identification.
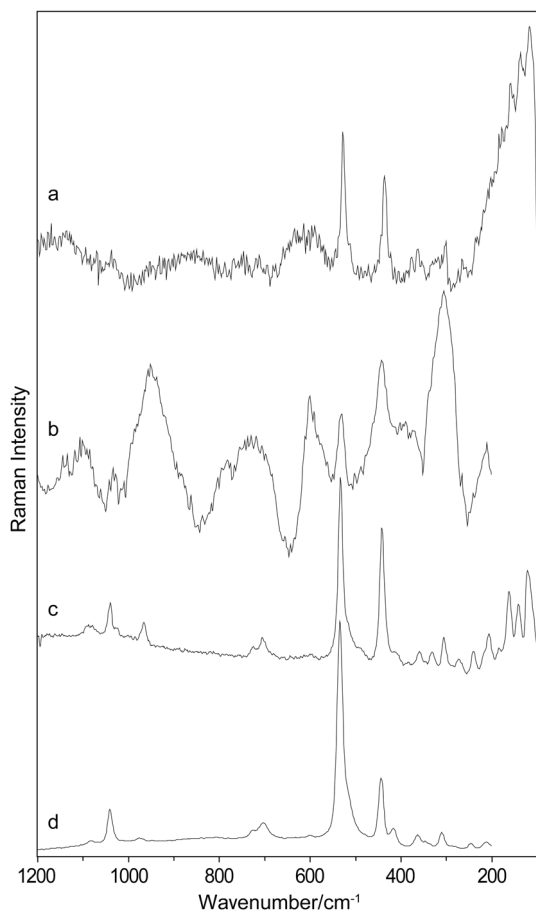

Figure 2. Raman spectra of natrolite obtained using the portable Raman spectrometers—baseline corrected spectra. Envawe 532 nm (a), Rigaku 532 nm (b), Envawe 785 nm (c) and DeltaNu 785 nm (d).
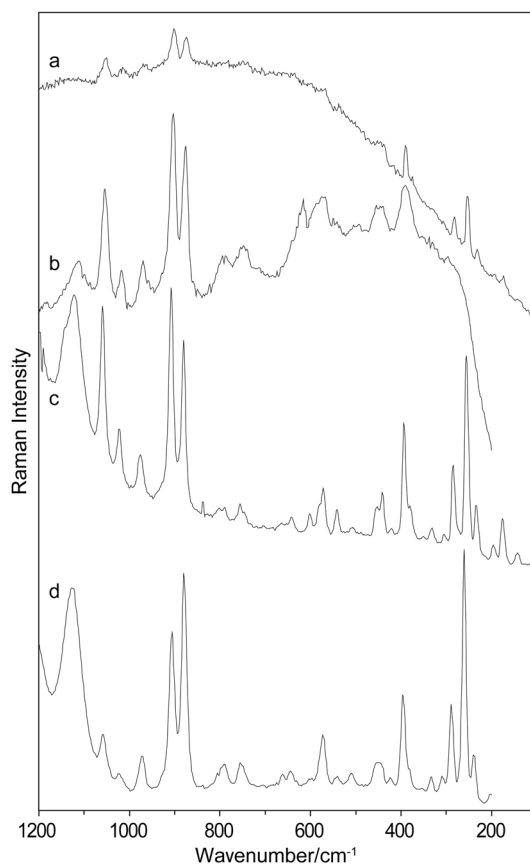

Figure 3. Raman spectra of euclase obtained using the portable Raman spectrometers—uncorrected baseline. Envawe 532 nm (a), Rigaku 532 nm (b), Envawe 785 nm (c) and DeltaNu 785 nm (d).

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Results and discussion

It was shown in previous reports that detection of minerals using portable Raman instruments can generally be achieved unambiguously and fast. This work was concerned with the identification of minerals from the following mineral groups: sulfates, carbonates, oxides and silicates. Critical issues of the successful application were identified as follows: absorption and fluorescence effects in the case of dark coloured minerals, measurements of very small grains in the frame of fine-grained rocks, as well as stable positioning. Here, we would like to estimate the performance of a given instrumentation where the 532-nm lasers are used.

Figures 2–4 present spectra obtained using different instruments and wavelength of excitation. Tables 3 and 4 summarize the Raman bands obtained analysing the minerals specimens using the handheld and portable instruments as well as comparisons with reference data from laboratory microspectrometer collected from Jehlička et al.[19] Here, information about the strongest bands found at correct positions $+/-3\,\mathrm{cm}^{-1}$ are reported (number of bands and wavenumbers).

Figures 2–4 show different Raman spectra of natrolite, euclase and phenakite obtained using the portable and handheld Raman spectrometers. Spectra of natrolite are reported as baseline-corrected, spectra of euclase as recorded. In both the figures, the two upper spectra are those obtained using the 532-nm excitation, the lower two those with 785-nm excitation.

Generally speaking the quality of spectra obtained is good or even excellent in the case of both the 785-nm cases: excellent S/N, acceptable baseline, the wavenumbers obtained differ $+/-2\,\mathrm{cm}^{-1}$ comparing to the reference values. Excellent coherence between

Table 3. Wavenumbers of Raman bands of zeolites and beryllium containing silicates recorded using the handheld Raman instruments (785 nm, 532 nm). For each instrument, in the first column, the number of unambiguously identified bands is reported. Wavenumbers of medium and strong bands of the strongest bands are given in additional eight columns. Values obtained using Raman microspectrometer (785 nm) are given for comparison

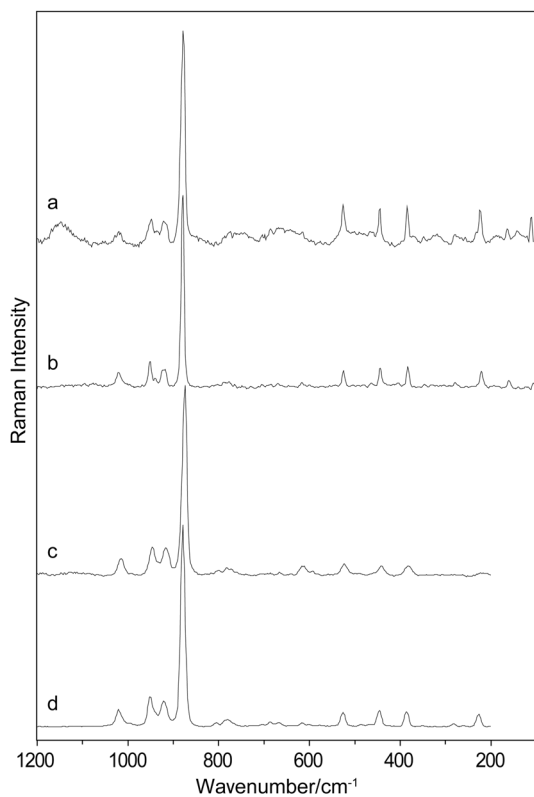| Mineral	Number	Raman bands observed In Via 785 nm, from[3]								Number	Raman bands observed 785 nm (Delta Nu)								Number	Raman bands observed 532 nm Rigaku							
Thomsonite	10	990	934	536	494	474	443	342	180	4	989	932	537	494	475	443	342	180	6	989	934	535	492	478	443	342	—
Stilbite	5	—	—	496	457	410	320	255	—	4	—	—	498	460	413	318	255	—	4	—	492	492	458	414	321	—	—
Natrolite	10	968	730	534	477	449	361	243	—	4	973	725	533	—	443	362	245	—	2	530	—	530	443	354	—	—	—
Euclase	10	908	882	602	573	395	322	259	—	6	907	881	572	396	289	260	—	—	4	904	877	576	—	390	—	—	—
Phenakite	12	950	923	878	615	525	444	383	230	8	950	919	878	616	525	447	385	228	7	946	918	876	614	523	441	381	—
Bavenite	7	945	544	505	448	348	295	140	—	7	944	545	506	451	350	331	285	1	1	—	503	—	—	—	—	—	—
Milarite	8	1126	834	538	479	436	382	288	161	7	1124	833	538	479	440	382	288	—	—	1118	—	—	—	476	—	—	—
Beryl	8	1065	1006	915	770	681	523	392	318	8	1064	1007	914	772	686	530	395	320	6	1064	1010	770	683	397	323	—	—

Figure 4. Raman spectra of phenakite obtained using the portable Raman spectrometers—uncorrected baseline. Envawe 532 nm (a), Envawe 785 nm (b), Rigaku 532 nm (c) and DeltaNu 785 nm (d).

(Figure: Raman Intensity versus Wavenumber/cm⁻¹, spectra labelled a, b, c, d; x-axis 1200 to 200.)

Table 4. Wavenumbers of Raman bands of zeolites and beryllium containing silicates using the dual portable Raman instrument (785 nm, 532 nm). For each excitation in the first column, the number of unambiguously identified bands is reported. Wavenumbers of medium and strong bands of the strongest bands are given in additional eight columns

In Via 785 nm, from [3]

Mineral	Number								
Thomsonite	10	990	934	536	494	474	443	342	180
Stilbite	5			496	457	410	320	255	
Natrolite	10	968	730	534	477	449	361	243	
Euclase	10	908	882	602	573	395	322	259	
Phenakite	12	950	923	878	525	444	383	230	
Bavenite	7	945	544	505	448	295	140		
Milarite	8	1126	834	538	479	436	382	288	161
Beryl	8	1065	1006	915	770	681	523	392	318

Raman bands observed 785 nm (Enwave)

Mineral									
Thomsonite	7	988	937	536	492	473	441	—	179
Stilbite	3			497	458	407		255	
Natrolite	5	967	725	533	442	359		243	256
Euclase	7	909	882	602	573	394		259	—
Phenakite	7	951	923	879	616	525	444	383	230
Bavenite	6	947	545	506	449	—	150		
Milarite	6	1124	538	478	381	286	158		161
Beryl	6	1070	687	318					

Raman bands observed 532 nm (Enwave)

Mineral									
Thomsonite	6	995	538	494	475	445	—	179	182
Stilbite	2		496			443			
Natrolite	2		533		443				
Euclase	6	908	583	574	395		256		259
Phenakite	6	881	920	—	525	445	—	384	
Bavenite	2		506	447					
Milarite	6	1123	536	479	383		158	163	
Beryl	6	1067	685				319	400	319

spectra obtained using the laboratory Raman microspectrometer and portable systems can be observed in the case of good Raman scatterers as in the case of euclase and phenakite. The worse situation can be seen for natrolite, even if also in this case the strongest bands are well recorded, however in this case sometimes weak and also non systematically shifted. In this case, an unacceptable difference up to around 9 cm^{-1} was observed using all the instruments tested. In Fig. 4a and b spectra from the dual spectrometer are reported showing the possibility of recording also the bands below 200 cm^{-1}, which is the advantage comparing to the Delta Nu spectrometer (6 bands at correct positions). Here, coherent detection of these minerals using instruments equipped by 785 nm confirms the previous report.[19]

The 532-nm equipped portable and handheld spectrometers used in this study perform more ambiguous results. In the case of the Rigaku handheld system, additional not-yet solved technical problems are behind artefacts observed. This can be seen in Fig. 1 where the strong wavy artefact feature, which is characteristic and omnipresent, occurs, generally on faint Raman scatterers. On the contrary, when studying other types of compounds, i.e. carotenoids, excellent and correct spectra are obtained. However, in this case, resonance Raman effects are observed allowing very good performance on such compounds. Sometimes, even the 532-nm excitation allows the acquisition of very good spectra and also correct identification. However, the difference between obtained wavenumbers and the reference values can exceed 3 cm^{-1}.

In Fig. 5 baseline uncorrected Raman spectra of milarite obtained with the 785-nm excitation are reported. The upper spectrum corresponding to the Enwave instrument is of good quality with Raman bands at correct positions (eight unambiguous bands). Interestingly it is possible to record also the bands below 200 cm^{-1}, which is the advantage comparing to the Delta Nu spectrometer (six unambiguous bands).

Few general conclusions can be noted comparing spectra reported here in Figs. 2–5 and comparing results in Tables 3 and 4. Both the instruments with near-infrared excitation can provide better
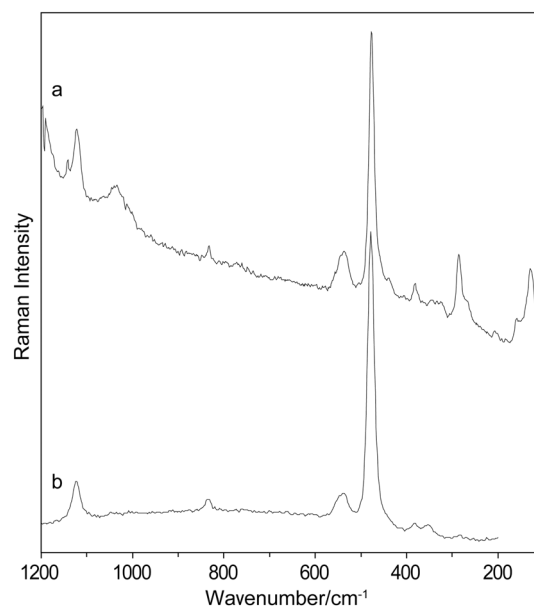

Figure 5. Raman spectra of milarite obtained using the portable Raman spectrometers—uncorrected baseline. Envawe 785 nm (a) and DeltaNu 785 nm (b).

quality spectra and higher number of Raman bands observed at correct $(+/-3\,cm^{-1})$ positions. This seems somehow unexpected as well as the problematic performance of the green laser excitation instrument. Testing of few other instruments is currently carried-out to better address the properties and technical features of those handheld systems.

Conclusions

Portable Raman spectrometers equipped with near-infrared-excitation diodes seems to be optimal instruments for discriminating zeolites and beryllium-containing silicates. Generally speaking, the main Raman bands of the investigated minerals are found at correct wavenumber positions, compared to the literature reference values and previous studies with lab Raman microspectrometers with excellent spectral resolution $(+/-\ 2\text{–}6\,cm^{-1})$. The portable Raman instruments tested in this study are useful tools for mineralogical purposes. This study complements previous investigations where Raman spectroscopy has been identified as a useful tool for identification of many minerals of different groups (sulphates, carbonates, silicates and organic minerals) outdoors and also in the frame of outcrops. Spectrometers allowing excitation with 532-nm lasers can also be used; however, their performance is clearly lower comparing to the 785-nm excitation. In this case some minerals can somehow ambiguously be identified using only few strongest Raman bands (this concerns namely bavenite, natrolite, and stilbite).

References

[1] J. Jehlička, P. Vítek, H. G. M. Edwards, M. D. Hargreaves, T. Čapoun, *J. Raman Spectrosc.* **2009**, *40*, 1082.
[2] J. Jehlička, P. Vítek, H. G. M. Edwards, M. D. Hargreaves, T. Čapoun *J. Raman Spectrosc.* **2009**, *40*, 1645.
[3] J. Jehlička, A. Culka, P. Vandenabeele, H. G. M. Edwards, *Spectrochim. Acta, Part A* **2011**, *80*, 36.
[4] P. Vitek, J. Jehlička, H. G. M. Edwards, *Appl. Spectrosc.* **2013**, *67*, 767.
[5] A. Culka, F. Košek, P. Drahota, J. Jehlička, *Icarus* **2014**, *243*, 440.
[6] J. Jehlička, H. G. M. Edwards, A. Culka, *Phil. Trans. Roy. Soc. A* **2010**, *368*, 3109.
[7] P. Vítek, E. M. A. Ali, H. G. M. Edwards, J. Jehlička, R. Cox, K. Page, *Spectrochim. Acta, Part A* **2012**, *86*, 320.
[8] A. Culka, J. Jehlička, P. Vandenabeele, H. G. M. Edwards, *Spectrochim. Acta, Part A* **2011**, *80*, 8.
[9] P. Vítek, J. Jehlička, H. G. M. Edwards, I. Hutchinson, C. Ascaso, J. Wierzchos, *Astrobiology* **2012**, *12*, 1095.
[10] J. Jehlička, A. Oren, *J. Raman Spectrosc.* **2013**, *43*, 1275.
[11] I. Miralles, S. E. Jorge-Villar, Y. Canton, F. Domingo, *Astrobiology* **2012**, *12*, 743.
[12] P. Vandenabeele, J. Jehlička, P. Vitek, H. G. M. Edwards *Planet. Space Sci.* **2012**, *62*, 48.
[13] P. Vandenabeele, H. G. M. Edwards, J. Jehlička, *Chem. Rev. Roy. Soc.* **2014**, *43*, 2628.
[14] W. P. Griffith, *J. Chem. Soc. A, Inorg. Phys.Theor.* **1969**, *9*, 1372.
[15] B. Wopenka, J. J. Freeman, T. Nikischer, *Appl. Spectrosc.* **1998**, *52*, 54.
[16] G. D. Gatta, V. Kahlenberg, R. Kaindl, N. Rotiroti, P. Cappelletti, M. de Gennaro, *Am. Mineral.* **2010**, *95*, 495.
[17] R. L. Frost, A. Lopez, L. Wang, A. W. Romano, R. Scholz, *Spectrochimica Acta Part A* **2015**, *137*, 70.
[18] I. Moroz, M. Roth, M. Boudeulle, G. Panczer, *J. Raman Spectrosc.* **2000**, *31*, 485.
[19] J. Jehlička, P. Vandenabeele, H. G. M. Edwards, *Spectrochimica Acta Part A*, **2012**, *86*, 341.
[20] D. Lauwers, A. G. Hutado, V. Tanevska, L. Moens, D. Bersani, P. Vandenabeele, *Spectrochim. Acta. A.* **2014**, *118*, 294.