Identification of tunnel structures in manganese oxide minerals using micro-Raman spectroscopy

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ABSTRACT

Manganese oxides have attracted the interest of many researchers due to their broad application field. These oxides possess various electrochemical, adsorption, and catalysis properties and are as such applied in the industrial context, e.g. steel industry, catalysis and removal of toxins in the ground or in waste water. In the archaeometrical field, manganese oxides have been used as pigments on various artefacts such as pottery and rock art paintings. The diversity of manganese oxide applications highlights the need for a well-defined Raman spectroscopic database with correct characterization of these compounds. However, identification of manganese oxides by Raman spectroscopy is not only challenging due to the wide variety of manganese oxides, but they are also weak Raman scatterers and are susceptible under the laser light. As such, characterization by Raman spectroscopy is not straight forward. In this research, we have focussed on seven natural, mineral (tunnel) samples which were identified by micro-Raman spectroscopy using two different laser wavelengths (785 and 532 nm). The experimental conditions were controlled to not introduce any modifications (degradation and/or phase transition) of the manganese oxide species. Both lasers have proven to be successful and were able to retrieve well characterized Raman spectra for each of the manganese oxide phase, which were compared with published literature.

KEYWORDS

Manganese oxides, tunnel structures, micro-Raman spectroscopy, mineral characterization, archaeometry

Introduction

Manganese oxides and oxyhydroxides are abundant in a variety of terrestrial and marine environments, typically as a consequence of supergene (weathering) and hydrothermal processes [1-4]. The most extensive deposition today is related to the formation of deep-sea manganese nodules [5] and manganese phases in soil [6,7].They are often found as black to brown finely-grained and poorly crystalline masses or coatings.

The occurrence of Mn oxides in natural systems is almost entirely controlled by chemical factors such as pH and redox potential (Eh), as well as the concentration of dissolved Mn in solution. Mn^{2+} is highly mobile under anoxic conditions and at low pH. In contrast, the Mn^{3+} and Mn^{4+} phases are only sparingly soluble and precipitate within the circumneutral pH range and oxidizing Eh [8]. Such conditions are characteristic for most surface waters, soils, and common rock weathering systems, leading to the secondary enrichment of $Mn^{3+/4+}$ oxides in these environments. The formation of Mn oxides usually starts with the oxidation of Mn^{2+}. However, the oxidation by O_2, despite being thermodynamically favorable, is kinetically very slow, and this reaction is probably catalyzed by microorganisms, particularly at low temperatures [9-11]. The bacteria-mediated Mn oxides are often poorly crystallized phylomanganates similar to vernadite ($(Mn^{4+},Fe^{3+},Ca,Na)(O,OH)_2 \cdot n\ H_2O$) or birnessite ($(Na,Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5\ H_2O$). Abiotic transformations and the maturation of initial disordered phases produce more crystalline Mn oxides [12,13]. In most Mn oxides, manganese occurs in octahedral coordination surrounded by oxygen atoms. The lattice then contains fundamental building units of $[MnO_6]$ octahedra that may share edges, corners, or faces, forming a wide variety of different structural arrangements. Two main topologies can be distinguished, chain or tunnel structures (tectomanganates) and layer structures (phylomanganates) [4,6]. It is generally accepted that tunneled Mn oxides are formed through topotactic transformation from layer-structured precursors, but this process requires high temperatures to reach a relevant rate, and therefore it applies mainly in hydrothermal setting [14-17]. At low temperature, characteristic for most of natural settings, this transformation is reported to be very slow [18]. Given the common occurrence of todorokite ($(Ca,K,Na,Mg,Ba,Mn)(Mn,Mg,Al)_6O_{12} \cdot 3H_2O$) in these systems, a different mechanism is probably responsible for its formation. Several possible pathways were investigated, including, for instance, biosynthesis [13,19] or complex repeated redox cycling [20], but the exact process and reaction conditions remain elusive.

Mn oxides are important environmental compounds as powerful oxidizing agents, as scavengers of important trace elements and reactive oxygen species, and as electron acceptors for anaerobic respiration [21]. Manganese (similar to iron) is a highly reactive soil constituent that is known to interact with organic compounds. Related to their high oxidation potentials, Mn oxides play a very important role in the distribution, transport, and transformation of other elements in the natural environment [7,22].

The manganese oxides have captured the interest of many scientists due to their multitude of applications in different fields [23,24]. In the industrial context, among other applications, manganese oxides have been used as additives for glass ware, steel industry [24,25]. Moreover, manganese oxyhydroxides and oxides are also recognized for their electrochemical, catalytic, magnetic and adsorptive properties [23,24,26-28]. It was demonstrated that Mn-based oxide nanomaterials are excellent adsorbents for the removal of heavy metals and pollutants [23]. Guo *et al.* in 2015 documented that MnOOH nanorods assisted in the superior removal of the toxic heavy metal arsenic from an aqueous environment [28].

The industrial applications represent only one of the numerous fields where manganese oxides can be employed. These oxides occur in nature mainly as black coloured minerals [24,29] and as such, manganese oxides have been used as pigments since antiquity [30]. Many researchers have encountered these pigments when studying historical artefacts [31-33].

Correct characterization of the different phases of manganese oxides are thus of great importance. Using a variety of techniques, identification of Mn oxides has been reported on natural mineralogical samples [29,34-36] as well as synthesized ones [26,34,37-39]. Xin *et al*. in 2022 synthesized seven Mn oxide/hydroxide samples which were characterized with a multi-instrumental approach, combining scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), laser induced breakdown spectroscopy (LIBS), Raman spectroscopy, mid-infrared (MIR) and very near infrared (VNIR) spectroscopy and powder X-ray diffraction (pXRD) [39].

Raman spectroscopy is one of the techniques widely used in the identification of such mineral structures [29,34-36,40,41]. Due to the versatility of manganese oxides as pigment in artefacts, Raman spectroscopy is a preferred technique owing to its non-destructive nature and its potential to be applied using mobile instrumentation [42].

The identification of manganese oxides with Raman spectroscopy has been challenging. A first drawback is that Mn oxides have been known to be weak Raman scatterers [34,35]. In order to enhance the Raman signal collection, one can increase the laser power and/or the acquiring measuring time. Moreover, due to their black colour, manganese oxides have a high absorption coefficient. Thus by applying greater laser power and/or measuring time, degradation effects and/or transformation of phases can occur. Which ultimately can hamper the correct identification of the unknown manganese oxide phases [29,34,35].

Nonetheless, Raman spectroscopy has been successfully applied for the identification of manganese oxide materials in the archaeometry field [33,43-45], as well as in the industrial applications [23,27,28] and the extra-terrestrial context [39]. Mulè *et al.* in 2017 made an automated curve fitting and unsupervised clustering of manganese oxide based on the Raman response of samples [25]. Bernardini *et al.* in 2021 investigated if the position of the ν(Mn-O) symmetric stretching vibration could help determine the oxidation state of manganese. They demonstrated that based on the Raman band position, an estimation of the oxidation state can be made and thus, can help determine which manganese oxide species is present [46].

Unfortunately, certain discrepancies are still encountered in literature when comparing Raman bands of specific manganese oxides. This is, for example the case for bixbyite α-Mn_2O_3. Its characteristic Raman band has been identified as a band around 580 cm^{-1} [40,46,47]. Others have characterized bixbyite by a broad band at *ca.* 700 cm^{-1} [29,37,39,48,49]. These inconsistencies can be due to degradation effects or impurities or chemical variations in the crystal structure of the manganese oxides.

All the above clearly underline the necessity for the construction of a well-defined Raman spectroscopy database for the correct characterization of Mn oxides, where the experimental parameters are carefully chosen as to not inflict any transformation and/or degradation of the manganese oxides under study here.

In the current research, seven natural manganese oxide minerals were successfully analysed with micro-Raman spectroscopy. The conditions were carefully selected not to hamper the spectral pattern due to degradation and/or transformation of the manganese oxides phases. The obtained Raman spectra were compared with the published literature on manganese oxide identification.

Materials and methods

Samples

A total of seven natural Mn oxide minerals were analysed in this study. Two were obtained from the collection of the Raman Spectroscopy group, Institute of Geochemistry, Charles University (Prague), i.e. a bixbyite specimen (about 2 cm) consisting of a black massive, heavy lustrous aggregate with quartz, and secondly, a jacobsite sample (about 6 cm) of a heavy, crystalline and highly lustrous massive aggregate in a quartzitic rock. In Figure 1, both minerals are depicted. The remaining five samples come from the collection of the Geology Department at Ghent University and were labelled as pyrolusite (sample 10248; unknown locality), hausmannite (sample 12575; Thüringen, Germany), manganite (sample 15535; Ilfeld, Harz Mts, Germany), pyrolusite (sample 10288; Canada), psilomelane (sample 13827; Saxony, Germany).

Table 1 gives an overview of the sample details, their chemical composition of the species and their corresponding oxidation states.

Raman Spectroscopy

The samples were measured using a confocal Bruker Optics *Senterra* micro-Raman spectrometer where an XYZ motorized stage is used for bringing the sample in the focal plane of an Olympus BX51 microscope. The microscope turret is equipped with objectives of magnifications of 5x (Numerical aperture (NA) 0.1), 20x (NA 0.4), 50x (NA 0.75) and 100x (NA 0.9). Spot sizes were visually estimated to be 50 µm, 10 µm, 4 µm and 2 µm, respectively. The dispersive Raman instrument is equipped with two lasers. A frequency doubled Nd:YAG laser of 532 nm and a diode laser of 785 nm. Neutral density filters are used to control the laser output on the sample. The power for the 532 and 785 nm laser ranges between 0.04 (1%) and 15.08 mW (100%) or 0.19

(1%) and 44.30 mW (100%) respectively. A thermoelectrically cooled charge-coupled-device operating at -65°C is used as detector. Spectral resolution of 3-5 cm^{-1} can be obtained, while the spectral range can vary between 60 and 3709 cm^{-1} and 80 and 3500 cm^{-1} for the 532 and 785 nm laser, respectively. The system is controlled by OPUS software (Bruker).

The samples were obtained as fragments. Small grains of the fragments were measured as such, requiring no sample preparation for obtaining the Raman spectra. Magnifications of 50x and 100x were used to focus the laser on to the minerals. Both lasers were used for characterization and identification of the mineral manganese oxide samples. The laser power was kept at the lowest (1%) with the neutral density filters, in order not to hinder correct identification based on degradation bands and patterns. The laser output on the manganese oxide samples was, 0.1 (50x) or 0.04 mW (100x) (532 nm laser), and 0.41 (50x) and 0.19 mW (100x) (785 nm laser). Other experimental parameters were: spectral resolution of 3-5 cm^{-1}, spectral range: 40-1540 cm^{-1} and 80-1520 cm^{-1} for the 532 and 785 nm laser respectively, while the confocal pinhole was kept at 50 µm. The obtained spectra were post-processed using the Thermo Grams/AU 8.0 suite software (Thermo Fischer Scientific).

Powder X-ray diffraction

To analyse the mineralogy of the samples, X-ray diffraction (XRD) was used. About 5 g of the samples were pulverized until all grains passed a 500 µm mesh sieve and further micronized (grain size of 10 µm or less) by wet grinding with ethanol using a McCrone Micronizing mill for micronisation. The obtained slurry was dried to obtain a powder for the XRD analysis. The XRD analyses were performed using a Bruker D8 Advance (current 25mA, voltage 40kV), equipped with a copper anode X-ray tube, at a 2 theta angle of 3° to 70°. The step size was set at 0,01° with a time per step of 48s.

The obtained spectra were analysed using X'Pert Highscore software (PANalytical) and the Joint Committee of Powder Diffraction Standards database (JCPDS) was used to identify the mineral phases present in the samples.

Results and discussion

In tunnel Mn oxides, edge-sharing [MnO_6] octahedra create single, double, or wider chains which are crosslinked through corner-sharing into a framework that encloses tunnels through the structure. In some cases, these tunnels are occupied by large cations (Ba, K, Pb, Ca, and others) and water molecules (e.g. the todorokite group) or can be generally small and inaccessible, as in pyrolusite (β-MnO_2) and ramsdellite (γ-MnO_2). The size of the tunnels is reflected in nomenclature of tunnel Mn oxides which is usually noted as m x n (for instance 1x1 or 3x3) reflecting the dimensions of the tunnel [50]. Manganese is mostly tetravalent (Mn^{4+}) in these oxides, although the substitution of Mn^{3+} and even Mn^{2+} for Mn^{4+} occurs extensively. Moreover, the open structures permits non-stoichiometry and the substitution of a variety of cations resulting in a wide structural and chemical variability of Mn oxides [4,51].

In the current research, the focus was on the correct identification and characterization of seven natural, mineral manganese oxides with tunnel structures.

To confirm the composition of the mineral samples and compare it against the Raman spectroscopy date, additional measurements were performed with powder X-ray diffraction. The obtained XRD results were in agreement with the Raman spectroscopy dataset and its interpretation.

In the following paragraphs, the analytical results for the Raman characterization are discussed.

Careful consideration was taken not to degrade the samples due to the sensitivity of the manganese oxides to the laser light and power. This led to measurements using the lowest laser power available. This however has as a consequence that many of the spectra were heavily affected by a weak signal-to-noise ratio. To circumvent this, longer accumulation time is used. However, these prolonged measurements have drawbacks. The increase in measuring time might have an influence on the degradation and/or alteration of the sample. For this, the samples were measured with gradually increasing measuring time in order to obtain the best signal-to-noise ratio. (Figure S1) Each obtained spectrum was evaluated against band shifting and broadening, as well as visual alteration, to obtain the optimal conditions.

For each manganese oxide phase, a table with the corresponding Raman wavenumbers is given. As well, a figure of the corresponding spectra with the two different lasers (785 and 532 nm) are given.

Pyrolusite (β-MnO_2)

Pyrolusite, β-MnO_2, is the most common manganese dioxide. It has a tunnel structure with a (1x1) tunnel framework [24,29,35]. The cavities that are formed by the shared edges of the MnO_6-octahedra are too small to encapsulate any large cations. The hydrogen cation, H^+, is however sufficiently small enough and as such might vacate these positions [24,29]. Pyrolusite has a rutile-type structure [29,35] and four Raman active modes ($1A_{1g}$, B_{1g}, B_{2g}, E_g) are expected [38,52]. The spectra (Figure 2), exhibit a clear band *ca.* 665 cm^{-1}, which is pronounced in both spectra, acquired with the two lasers. However, a difference can be observed in the spectra from the 785 nm versus the 532 nm laser. In the latter one, a band *ca.* 535 cm^{-1} has an increased intensity compared to the spectrum obtained with the 785 nm laser. Here, only a weak and broad band appears *ca.* 540 cm^{-1}. Additionally, a small band around 760 cm^{-1} is also present in the 532 nm laser spectrum. In the 785 nm spectrum, we see a band at *ca.* 740 cm^{-1}. This band is reported to be orientation and polarization dependent [29,35]. A last Raman active mode is expected at the low wavenumber and is of low intensity in analogy with rutile-type oxides [29,48]. In the spectrum obtained with the 785 nm laser, a broad band *ca.* 120 cm^{-1} can be observed.

It must also be noted that both spectra show a vast amount of noise. The manganese oxides, especially pyrolusite, are weak Raman scatterers. As such, the signal-to-noise ratio is rather low for these species. It has been documented that this is due to the quasi metallic state of pyrolusite [34].

The measured spectra largely agree with those available from literature [29,34,35,38,39]. However, some published data report a band at *ca.* 580 cm^{-1} [40,41,53], the origin of which has been debated [29]. It must be considered that pyrolusite, as a black coloured manganese oxide, is susceptible to the laser power and as such can degrade. Hence, this band has been characterized by some as resulting from a degradation product of pyrolusite, i.e. bixbyite α-Mn_2O_3 [35,46]. The latter phase is formed when pyrolusite is heated at temperatures above 450°C [54,55]. Another group of researchers have described this aforementioned band to ramsdellite γ-MnO_2. This polymorph of pyrolusite is known to form intergrowths in pyrolusite [29]. Gao *et al.* (2008) reported that a Raman spectrum of pyrolusite sample cannot have more than four bands. If extra bands are arising, they originate from impurities in the sample [38].

In Table 2, the identified Raman wavenumbers for our two samples of pyrolusite are compared to published data.

Manganite (γ-MnOOH)

There are three natural polymorphs of manganese oxyhydroxide, namely groutite (α-MnOOH), feitknechtite (β-MnOOH) and manganite (γ-MnOOH), of which the latter is the most abundant mineral [24,56]. Manganite is isostructural with pyrolusite and when it is heated above 300°C, it transforms to pyrolusite [56]. In the MnO_6-octahedra, some of the oxygen atoms are replaced by a hydroxide ion OH^-. As such, the Mn^{4+} ions are reduced to Mn^{3+} to compensate for additional charges. This reduction however induces structural effects for the octahedral building blocks. Mn^{3+} ions are affected by the Jahn-

Teller effect, giving rise to distorted $Mn^{3+}O_6$-octahedra. The distorted structure is even more pronounced due to hydrogen bonding associated with the hydroxide ions [24,29,56]. The effect of the distortion is reflected by six different Mn-O bond distances in the octahedra compared to the two bond distances present for pyrolusite. In addition, this reduces the symmetry of the manganite structure [56]. In contrast, the distorted structure gives rise to a Raman spectrum with more defined bands [29,35].

In Figure 3, manganite Raman spectra show bands at lower wavenumbers compared to pyrolusite, which are an effect of the longer bonds in the distorted structure [29,35]. Both lasers used (785 and 532 nm) have proven to be able to characterize the γ-MnOOH sample. The only notable difference between the spectra recorded with the two lasers is a change in intensity of the band at *ca.* 622 cm^{-1}.

Comparing our measured sample with literature data (Table 3), shows a large similarity between the reported values.

Bixbyite (α-Mn_2O_3)

Trivalent Mn oxide can occur in two structural forms; α-Mn_2O_3 bixbyite, or γ-Mn_2O_3. Only the former occurs in nature [24]. The structural form of bixbyite is quite unique and that has attracted a lot of attention with respect to attempt and mimic this structure in the use for catalysis and coatings [57-60]. Bixbyite is a more stable compound than pyrolusite. Heating the latter to over 450°C induces the transformation. When α-Mn_2O_3 is in turn heated to up to 1000°C, it transforms to hausmannite, the most stable form of manganese oxide [33,55,61,62].

Bixbyite is a phase with an ambiguous Raman spectroscopic identification. Its characterization can be defined in two groups. One of which includes a high intensity band *ca.* 580 cm^{-1} [40,46,47], whereas another classification assigns it with a band at *ca.* 700 cm^{-1} [29,37,39,48,49].

Shown in Figure 4, bixbyite spectra are defined by very broad bands and a rather intense background signal. Well-defined, high intensity bands are not visible for this mineral. Our spectra are in line with mineral spectra reported [29] and on synthetic bixbyite samples [39,48,49]. An overview of the reported Raman wavenumbers for bixbyite can be found in Table 4.

Hausmannite (Mn_3O_4)

Hausmannite is the most stable manganese oxide with a tetragonal distorted spinel structure [24,29,35]. It has Mn in an uniquely mixed valence state, which is a combination of $Mn^{2+}O_4$ tetrahedra and $Mn^{3+}O_6$ octahedra [24,29,35]. The compound is considered as stable under laser light, and, as such, the identification and characterization of hausmannite with Raman spectroscopy is rather straightforward. The obtained Raman spectra as recorded with the 785 nm and 532 nm laser are shown in Figure 5. Both lasers yielded a spectrum with a good signal-to-noise ratio and only a slight difference in intensity of the lower wavenumber bands can be noticed. The measured Raman bands are listed in Table 5 and are in good agreement with previously reported values. A slight shift in wavenumbers can be explained by the difference in grain size between the analysed samples [63].

Psilomelane

Psilomelane is an obsolete and generic name for a wide variety of manganese oxides. Many of the Mn oxides which were previously identified as “psilomelane” are now characterized as α-MnO_2. This group of manganese oxides, often called the hollandite group, are dioxides which have a two tunnel structure. The larger tunnel structures are (2x2) and can encapsulate various divalent as well as univalent cations. The smaller framework tunnels (1x1) are left vacant [24,26,29,35,38,39,48]. The extra charge induced by the participation of the tunnel cations is counteracted by the reduction of

Mn^{4+} to lower valence cation Mn^{3+}, hence some of the octahedra are distorted due to the Jahn-Teller effect [24,29,38]. Sometimes, aluminium or iron can be found in the framework as well [29]. The different phases of this group of manganese oxides are characterized by their principal cation in the tunnel framework, and each form has a different mineral name: Ba^{2+} in hollandite, K^{+} in cryptomelane, Sr^{2+} in strontiomelane, Pb^{2+} in coronadite and Na^{+} in manjiroite [24,29]. The hollandite group of manganese oxides all have a framework of equal [MnO_6] octahedra, and as such, the Raman spectra for these components are similar. Minor variations can be attributed to the chemical environment differences introduced by the different cations. Generally, the spectral band pattern of the hollandite group is characterized by two strong bands *ca.* 630 and 580 cm^{-1}, a medium intensity band *ca.* 515 cm^{-1} and a band *ca.* 180 cm^{-1} in the lower wavenumber region [29,39,48]. Post *et al.* calculated that modes due to tunnel cations movements are found below or at 100 cm^{-1}. Observations in this region however are met with some technical challenges due to the cut off notch filter and/or strong Rayleigh scattering, making it difficult to differentiate between the different phases [29].

Another type of manganese oxides that was frequently labelled as “psilomelane” is romanéchite. This is a hydrated barium manganese oxide consisting of double and triple chains of Mn-O octahedra, with (2x3) tunnels. In these tunnels Ba^{2+} cations and water molecules arrange themselves in a 1:2 ratio [29,35]. The tunnel lattice is similar to that of the hollandite group and a comparable spectrum is obtained with Raman spectroscopy. Nonetheless, a differentiation between romanéchite and the hollandite-group can be made based on the rather intense band at lower wavenumbers. This band is found at 150 cm^{-1} for romanechite whereas for the hollandite-group, this band is shifted to a higher wavenumber (~180 cm^{-1}) [29].

For our “psilomelane” sample, the typical pattern for α-MnO$_2$ spectrum can be recognized (Fig. 6) with a band at *ca.* 630 cm^{-1} and 580 cm^{-1}. For more exact identification, other Raman bands wavenumbers should be taken into account. Romanéchite cannot be the origin for this Raman band pattern as a band *ca.* 148 cm^{-1} is not observed in the spectrum, nor a band *ca.* 730 cm^{-1} [29,35]. One could argue that a weak band is present *ca.* 740 cm^{-1} in both spectra displayed (Fig. 6). However, the band *ca.* 730 cm^{-1} is quite intense when measured with the 785 nm laser [29]. This suggests that the measured “psilomelane” is a member of the hollandite group. In hollandite, the Raman band around 630 cm^{-1} is usually more pronounced as a shoulder instead of an individual band [29,35]. The spectra obtained here, are indicative of cryptomelane[29,39,48]. This result is confirmed by the powder X-ray diffraction which was performed on the sample, showing the pattern of cryptomelane. (Fig. S2) Some coronadite traces were also identified with pXRD, however these were not identified with Raman spectroscopy. In Table 6, a comparison of the Raman band positions is given for the manganese oxide cryptomelane.

Jacobsite

Although jacobsite cannot be considered as a pure manganese oxide, it is however of interest within an archaeological context related to pigments.

Jacobsite is in fact a mixed transition metal oxide composed of iron and manganese. As both elements are chemically similar, manganese and iron can readily substitute. The chemical composition of jacobsite can hence vary as both divalent and trivalent Mn and/or Fe can be present in varying ratio’s [43,64]. Jacobsite can thus be described by the following composition: $(Mn^{2+}, Fe^{2+})(Mn^{3+},Fe^{3+})_2O_4$ [33,43].

Jacobsite is interesting from an archaeological perspective due to its specific use. For example, it has been used as a pigment for applying dark coloured decoration on pottery [33,44,45]. The specific pigment used can come from natural jacobsite, but it can also be derived synthetically by combining a manganese oxide, e.g. pyrolusite, with an iron oxide phase, such as haematite (α-Fe_2O_3). In the latter case, at elevated temperatures a transformation occurs. In a first step, pyrolusite is reduced to form bixbyite, α-Mn_2O_3 at a temperature of around 450°C [54,65] and when the temperature is elevated even more, bixbyite and haematite react to form jacobsite [33,43,44]. The preparation of this pigment by combing two natural oxides has been known since antiquity [30]. A correct characterization of this phase can thus help unravel archaeological questions on this matter and gain insight in production processes.

As jacobsite has the same structure as hausmannite, similar Raman spectra are expected. In Figure 7, the spectra for the analysed jacobsite sample are shown. At first glance, a more or less similar spectrum as that of hausmannite (Figure 5) can be observed, with a strong Raman band at the higher wavenumbers (600-700 cm^{-1}) and some smaller Raman band features located at lower wavenumbers (300-500 cm^{-1}). However, a shift in Raman band position is noticeable.

As the chemical composition of jacobsite fluctuates based on the iron/manganese substitution levels, the reported wavenumbers values for jacobsite vary [33,43,66]. Clark *et al.* analysed a natural mineral jacobsite sample from the Natural History Museum in London and identified the Raman bands located at 640, 470 and 339 cm^{-1} [66], whereas Graves *et al.* performed Raman spectroscopy on a synthetic sample with reported bands at: 625, 543, 496 and 331 cm^{-1} [64]. Buzgar *et al.* related the position of the characterizing band (~630 cm^{-1}) on the Fe substitution: with higher amounts of iron, the band is shifted towards higher wavenumbers of *ca.* 640 cm^{-1}, with a higher ratio of manganese, the band is *ca.* 620 cm^{-1} [43]. Hence, a variation of around 20 cm^{-1} is possible in this context.

In our spectra (Figure 7), the main characteristic band is positioned at 610 cm^{-1}, falling outside the range for jacobsite. However, with similar chemical properties, substitution of magnesium should also be taken into account as it can be incorporated into the crystal lattice relatively easily. Its effect is a shift in Raman band position towards lower wavenumbers, i.e. *ca.* 600 cm^{-1} [33,43]. Therefore, we suspect that the sample we have characterized as jacobsite would contain a significant amount of magnesium and can be labelled as Mg-jacobsite. When comparing the spectra obtained with the 785 nm versus the 532 nm laser, a difference at the lower wavenumbers can be discerned. The intensity of these bands is more pronounced with the 785 nm laser. In both spectra a shoulder is observed *ca.* 680 cm^{-1}, the origin of which is still unclear, but it might be due to cation disordering and partial inversion of the spinel structure [67].

In Table 7, an overview of Raman wavenumbers for different species of jacobsite are tabulated.

Conclusion

Micro-Raman spectroscopy has proven to be able to identify and characterize tunnel structures in manganese oxides. No modifications (degradation and/or transformation) were inflicted on the studied manganese oxide samples with the current experimental parameters. Both the 785 and the 532 nm laser have successfully obtained spectra with well-defined bands. Some intensity differences can be noted between spectra with the two different lasers, nonetheless each laser can acquire a spectrum with identifiable bands for each manganese oxide phase. The Raman band positions for each of the manganese oxide sample was compared with the published data and found to be in agreement with the literature.

Acknowledgments

The authors wish to express their gratitude towards Dr. Dimitri Vandenberghe for his help with collecting the mineral samples, as well as Sylvia Lycke for her help with Raman analysing the manganese oxide samples. We like to thank both Ann-Eline Debeer and Veerle Vandenhende for their help with the powder X-ray diffraction analysis. Dr. A. Rousaki greatly acknowledges the special research fund of Ghent University (UGent-BOF), for her post-doctoral grant.

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Figure captions

Figure 1 Photographs of two of the analysed manganese oxides; (a) bixbyite Mn_2O_3 and (b) jacobsite $FeMn_2O_4$.

Figure 2 Raman spectra of the mineral sample pyrolusite β-MnO_2 acquired with 532 (top) and 785 (bottom) nm laser. Measuring conditions were 30 acc. of 60 s, 50x, NA: 0.75 (4 µm spot size). The power of the 532 and 785 nm laser were 0.1 mW and 0.41 mW, respectively.

Figure 3 Raman spectra of the mineral sample manganite γ-MnOOH. Measuring conditions for the 532 nm and 785 nm laser, were 60 acc. of 30 s, 50x, NA: 0.75 (4 µm spot size), 0.1 mW and 40 acc. of 60 s, 50x, NA: 0.75 (4 µm spot size), 0.41 mW, respectively.

Figure 4 Raman spectra of the mineral sample bixbyite α-Mn_2O_3. Measuring conditions were: 60 acc of 90 s, 50x, NA: 0.75 (4 µm spot size), 785 nm laser, 0.41 mW and 40 acc of 60 s, 50x, NA: 0.75 (4 µm spot size), 532 nm laser, 0.1 mW.

Figure 5 Raman spectra of the mineral sample hausmannite Mn_3O_4 acquired with 532 (top) and 785 nm laser (bottom). The experimental parameters are 3 acc. of 30 s, 50x, NA: 0.75 (4 µm spot size), 0.41 mW and 15 acc. of 10 s, 50x, NA: 0.75 (4 µm spot size) for the two lasers respectively, 0.1 mW.

Figure 6 Raman spectra of the mineral sample psilomelane. The mineral was identified as cryptomelane $K(Mn^{4+}_7,Mn^{3+})O_{16}$ and the spectra were measured under the following experimental conditions. For the 532 and 785 nm laser, the parameters were: 60 acc of 30 s, 50x, NA: 0.75 (4 µm spot size), 0.1 mW and 30 acc of 60 s, 50x, NA: 0.75 (4 µm spot size), 0.41 mW.

Figure 7 Raman spectra of the mineral sample jacobsite $FeMn_2O_4$. The spectra were obtained with the following experimental conditions: 30 acc of 60 s, 50x, NA: 0.75 (4 μm spot size), 532 nm, 0.1 mW and 3 acc of 60 s, 50x, NA: 0.75 (4 μm spot size), 785 nm, 0.41 mW.

Table captions

T1 Overview of the sample sites of the manganese oxide mineral samples with their chemical composition and manganese oxidation state.

T2 Raman wavenumbers of the manganese oxide mineral pyrolusite β-MnO_2 in comparison with literature data.

T3 Raman wavenumbers of the manganese oxide mineral manganite γ-MnOOH in comparison with literature data.

T4 Raman wavenumbers of the manganese oxide mineral bixbyite α-Mn_2O_3 in comparison with published data.

T5 Raman wavenumbers of the manganese oxide mineral hausmannite Mn_3O_4 in comparison with reported data.

T6 Raman wavenumbers of the manganese oxide mineral cryptomelane $K(Mn^{4+}_7,Mn^{3+})O_{16}$ in comparison with literature data.

T7 Raman wavenumbers of the manganese oxide mineral jacobsite $FeMn_2O_4$ in comparison with published data.

Tables

T1

Name	***Chemical composition***	***Oxidation state Mn***	***Origin***
Pyrolusite	β-MnO_2	Mn^{4+}	Unknown location
Pyrolusite	β-MnO_2	Mn^{4+}	Canada
Bixbyite	α-Mn_2O_3	Mn^{3+}	Unknown location
Jacobsite	$FeMn_2O_4$	Mn^{2+}, Mn^{3+}	Unknown location
Manganite	γ-MnOOH	Mn^{3+}	Ilfeld, Harz Mountains, Germany
Psilomelane	Unknown	Unknown	Saxony, Germany
Hausmannite	Mn_3O_4	Mn^{2+}, Mn^{3+}	Thüringen, Germany

T2

Manganese oxide mineral	***Wavenumber/cm^{-1}***	***Type***	***Reference***
Pyrolusite β-MnO_2	760, 665, 535	Natural	Current study
	668, 538	Natural	Current study
	760, 664, 535, 121	Natural	[29]
	750, 665, 538, 486, 377, 319	Synthetic and natural	[34]
	755, 661, 532	Natural	[35]
	750, 667, 538	Synthetic	[48]

T3

Manganese oxide mineral	***Wavenumber/cm^{-1}***	***Type***	***Reference***
Manganite γ-MnOOH	622, 557, 530, 492, 387, 357, 283, 257, 218, 147	Natural	Current study
	620, 554, 527, 384, 356, 253, 216	Synthetic	[23]
	660, 623, 557, 533, 494, 388, 358, 284, 257, 147	Natural	[29]
	621, 558, 531, 492, 386, 358, 283, 259, 218	Natural	[35]
	620, 555, 528, 388, 358	Natural	[40]
	734, 623, 558, 530, 492, 389, 360, 266	Synthetic	[48]

T4

Manganese oxide mineral	***Wavenumber/cm^{-1}***	***Type***	***Reference***
Bixbyite α-Mn_2O_3	700, 544, 330, 190, 146	Natural	Current study
	700, 545, 394, 315, 195, 126	Natural	[29]
	698, 645, 592, 481, 404, 314, 192	Natural and synthetic	[34]
	703, 654, 626, 586, 538, 418, 318, 200, 126	Synthetic	[39]
	690, 396, 305	Synthetic	[48]

T5

Manganese oxide mineral	***Wavenumber/cm^{-1}***	***Type***	***Reference***
Hausmannite Mn_3O_4	659, 375, 319, 291	Natural	Current study
	659, 476, 370, 319, 290	Natural	[29]
	653, 579, 485, 357, 310	Natural and synthetic	[34]
	658, 479, 375, 320, 292	Natural	[35]
	657, 480, 375, 320, 291	Synthetic	[48]
	676, 373, 319	Synthetic	[63]

T6

Manganese oxide mineral	***Wavenumber/cm^{-1}***	***Type***	***Reference***
Cryptomelane K^+-α-MnO_2	740, 630, 580, 513, 388, 287, 205, 180	Natural	Current study
	631, 584, 514, 503, 466, 391, 328, 282, 203, 184	Natural	[29]
	750, 644, 580, 524, 476, 391, 334, 184	Synthetic	[39]
	753, 634, 578, 512, 386, 330, 183	Synthetic	[48]

T7

Manganese oxide mineral	***Wavenumber/cm^{-1}***	***Type***	***Reference***
Mg-Jacobsite $(Mg,Fe)Mn_2O_4$	680, 610, 437, 326, 179, 126	Natural	Current study
Jacobsite $FeMn_2O_4$	625	Natural	[43]
	625, 543, 496, 331	Synthetic	[64]
	640, 456, 339	Natural	[66]
	640-620	Natural	[67]