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Infrared spectroscopic study of the synthetic Mg-Ni talc series

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Abstract

Five talc samples ($(\text{Mg,Ni})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) covering the entire Mg-Ni solid solution were synthesized following a recently developed and patented process (Dumas et al. 2013a, b), which produces sub-micron talc particles replying to industrial needs. Near- and mid-infrared spectra were collected and compared to infrared spectra modeled from first-principles calculations based on density functional theory. The good agreement between experimental and theoretical spectra allowed assigning unambiguously all absorption bands. We focused in particular on the four main OH stretching bands, which represent good probes of their local physical and chemical environment. The description of the vibrational modes at the origin of these absorption bands and the theoretical determination of absorption coefficients provide a firm basis for quantifying the talc chemical composition from infrared spectroscopy and for discussing the distribution of divalent cations in the octahedral sheet. Results confirm that these synthetic talc samples have a similar structure as natural talc, with a random distribution of Mg and Ni atoms. They only differ from natural talc by their hydrophilic character, which is due to their large proportion of reactive sites on sheet edges due to sub-micronic size of the particles. Therefore the contribution on infrared spectra of hydroxyls adsorbed on edge sites has also been investigated by computing the infrared signature of hydroxyls of surface models.

Keywords: Talc, hydrothermal synthesis, Infrared spectroscopy, first-principles calculation, DFT.

1. Introduction

Talc is a trioctahedral phyllosilicate with the structural formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. A representation of its structure can be found for instance in Dumas et al. (2015), where we see the octahedral sheet containing Mg atoms sandwiched by two tetrahedral sheets containing Si atoms. In talc, each hydroxyl group is bonded to three octahedral cations (Mg) and is oriented perpendicular to the (*ab*) plane (i.e., plane defined by talc sheets).

Natural talc is used in many industrial applications, in particular as filler in composite materials in order to reduce the production costs and possibly to improve their physical and chemical properties (Claverie et al. 2017). However, natural talc has important limitations. It contains minor or trace elements (Martin et al. 1999), and is often associated with other minerals like chlorite, chrysotile, pyrite, graphite, calcite or amphibole. Furthermore, industrial applications usually require small and homogeneous particles. This cannot be achieved by grinding natural talc since the crystal structure becomes amorphized. These limitations were circumvented by developing a new process to synthesize sub-micron talc particles (Dumas et al. 2013a, b, 2016; Claverie et al. 2017). These syntheses produce a single-phased chemically pure product from a short hydrothermal treatment (from a few seconds to few hours). Providing talc products of accurately controlled chemical compositions, and at the same time, an inexpensive and convenient method to verify this composition would increase the industrial applications. In this aim, we investigate here the Mg-Ni series by infrared spectroscopy, building on the work by Dumas et al. (2015). This previous study focused on the transformation mechanism from the amorphous talc precursor to crystalline synthetic talc, using samples with 50% and 100% Ni substitution.

We report here the infrared spectroscopic investigation of synthetic talc samples with five compositions spanning the entire Mg-Ni solid solution. The measured spectra are discussed in light of the modeling of the infrared spectra of Mg-Ni talcs from first-principles

calculations based on the density function theory. A special attention is given to the absorption bands related to OH stretching vibrations in the near- and mid-infrared regions, since OH groups of talc are known to be a good probe of the local chemical environment (e.g., Wilkins and Ito 1967; Petit et al. 2004; Martin et al. 2006). Since the pioneer work of Wilkins and Ito (1967), the four OH absorption bands observed in binary octahedral solid solutions of talc are assigned to OH groups characterized by their specific cationic environment. These bands can be used to derive the chemical composition of talc and to discuss the distribution of the magnesium and the substituting ion between the two crystallographically distinct octahedral sites. The present theoretical modeling of infrared spectra provides new insights on these applications. Sub-micron talc particles are characterized by a large proportion of edge surfaces with many reactive sites. This explains the observed hydrophilic character of synthetic talc compared to the well-know hydrophobicity of natural talc (Dumas et al. 2013c, 2016; Claverie et al. 2017). In order to improve our understanding of the infrared spectra of synthetic talcs, we also modeled the infrared signature of OH and H₂O adsorbed on particle edge sites.

2. Materials and methods

2.1 Samples preparation

The starting materials for the co-precipitation experiments were magnesium acetate tetrahydrate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), sodium acetate trihydrate ($\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$), and acetic acid. All reagents were purchased from Aldrich and used

without any further purification. A 1N solution of glacial acetic acid was prepared using deionized water.

Five samples of synthetic talc (labeled Ni0, Ni25, Ni50, Ni75 and Ni100, according to the mol % Ni targeted) were prepared using the process describes in patent of Dumas et al. (2013a. b). Synthetic talc preparation was achieved in two steps. First, a talc precursor was prepared at room temperature and atmospheric pressure with the right (Mg+Ni)/Si talc ratio (Table 1). Second, a hydrothermal treatment at 300 °C and 86 bar during 6 h transformed the precursor into synthetic talc. Before analysis, samples were centrifuged and rinsed to remove any traces of sodium acetate salt.

2.2 Characterization

X-ray diffraction analysis (XRD) was performed on dried talc powders using the side-loading procedure to minimize preferential orientations. The XRD patterns were recorded on a Bruker D2 Phaser diffractometer over the 0-80°2 θ CuK α_{1+2} angular range, with a step size of 0.02°2 θ and a 0.5 s count time per step.

The Fourier transformed infrared spectroscopy in the near-infrared region was recorded with 32 scans at a resolution of 4 cm⁻¹ between 4,000 and 10,000 cm⁻¹ using a Thermo Nicolet 6700 FTIR spectrometer (Services Communs de Chimie, UPS, University of Toulouse) with a smart NIR Integrating Sphere (CaF₂ beam splitter and InGaAs detector). No specific sample preparation was needed.

Mid-infrared spectra were recorded with a Thermo Nicolet 6700 FTIR spectrometer equipped with a DLaTGS detector using a transmission mode. The spectral conditions consisted in a resolution of 4 cm⁻¹ between 400 and 4,000 cm⁻¹ using 16 scans. Sample powders were diluted into KBr pellets.

Regions of OH stretching modes were analyzed using the Fityk program (Wojdyr 2010) to decompose the infrared signal into pseudo-Voigt components. The baseline was defined around the two regions where vibrational modes are related to structural OH groups (i.e., 6900-7300 cm^{-1} in near-infrared and 3610-3730 cm^{-1} in mid-infrared, respectively). During the decomposition, the number of components was kept as minimal as possible.

2.3 Computational methods

Structural relaxations and calculation of vibrational properties were performed within the framework of the density functional theory (DFT), using periodic boundary conditions and the generalized gradient approximation (GGA) to the exchange-correlation functional, with the PBE parameterization (Perdew et al. 1996). The ionic cores were described using the latest version of ultrasoft pseudopotentials from the GBRV library (Garrity et al. 2014). Wave functions and charge density were expanded in plane-waves with 40 and 240 Ry cutoffs, respectively, corresponding to a convergence of the total energy better than 1 mRy/atom. For the electronic integration, the Brillouin zone of the triclinic talc unit cell (space group *C-1*) was sampled using a shifted $4 \times 2 \times 2$ *k*-points grid. For Ni-bearing talc, calculations were spin-polarized and set up to the ferromagnetic structure. The structure relaxations and vibrational mode calculations were done using the PWscf and PHonon codes of the Quantum ESPRESSO package (Giannozzi et al., 2009; <http://www.quantum-espresso.org>). During the relaxations, forces on atoms were minimized to less than 10^{-4} Ry/a.u. Transmission infrared spectra were calculated using an electrostatic model similar to the one developed by Balan et al. (2001, 2008). This approach is based on the *ab initio* calculation of the low-frequency dielectric tensor, which requires the frequencies and atomic displacements of the normal vibrational mode and dielectric quantities (Born effective charges and electronic dielectric tensor), all computed within the harmonic approximation using the linear response theory

(Baroni et al. 2001) as implemented in the PHonon code. In order to avoid the divergence of the low-frequency dielectric tensor at the resonance frequencies, we used a damping coefficient arbitrarily fixed to 2 cm^{-1} (cf Equation 1 of Balan et al. 2001).

Talc unit cell contains six Mg atoms in the octahedral sheet. In order to investigate the Mg-Ni series, starting from this pure Mg-talc, we substituted one, three, five or six Mg atoms by Ni atoms, leading to structural models corresponding to talcs with Ni concentrations of 0.0, 16.7, 50.0, 83.3 or 100.0 mol %, respectively (the theoretical models were labeled Ni0, Ni17, Ni50, Ni83 and Ni100, respectively).

In addition to the investigation of the vibrational properties of bulk Mg-Ni talcs, we also explored the infrared signature of hydroxyl groups and water molecules remaining adsorbed on edge sites of small talc particles even after drying of talc powders. To this aim, we also built two surface models (surfaces (100) and (010)) for the two end members of the Mg-Ni series. We adopted a supercell approach, in which a slab bounded by either (100) or (010) surfaces was cut from the optimized bulk structure of either Mg-talc or Ni-talc. Slabs were cut in a manner for preserving the tetrahedral coordination of Si atoms and the octahedral coordination of Mg or Ni atoms. Protons were then added to surface O atoms in order to compensate the O charge, which leads to neutral slabs containing 92 or 99 atoms for the (010) or (100) surfaces, respectively. The slab surfaces were separated from their adjacent images by a vacuum gap of at least $9 \text{ \AA}$. The four triclinic simulation cells have the following X, Y, Z dimensions: $21.40 \text{ \AA}$, $9.27 \text{ \AA}$, $10.12 \text{ \AA}$ for the (100) surface of Mg-talc, $5.35 \text{ \AA}$, $27.80 \text{ \AA}$, $10.12 \text{ \AA}$ for the (010) surface of Mg-talc, $21.31 \text{ \AA}$, $9.24 \text{ \AA}$, $9.67 \text{ \AA}$ for the (100) surface of Ni-talc, and $5.33 \text{ \AA}$, $27.72 \text{ \AA}$, $9.67 \text{ \AA}$ for the (010) surface of Ni-talc. Surface relaxation was performed at constant volume and with a Brillouin zone sampling reduced to a single point in the direction perpendicular to the surface. Vibrational properties were computed only for OH stretching modes.

3. Results and discussion

3.1 Structural properties

X-ray diffraction patterns were collected on the five synthetic talc samples (Fig. S1). Each pattern shows inter-reticular distances characteristic of 001, 003 and 02 l -11 l reflections of talc structure (e.g., Dumas et al. 2015). No other mineral phase is detected. One can note that 001 and 003 peaks become sharper and more intense with increasing Ni content, which reflects a progressive increase in the crystallinity degree, as previously observed by Martin et al. (1992).

Table 2 compares the experimental and DFT-optimized values of cell parameters and mean bond lengths for the Mg end member of talc. In our calculations, a and b cell parameters are overestimated by 1% while α , β , γ angles are slightly underestimated by less than 0.4%. These trends are similar to those observed by Ulian et al. (2013). The only discrepancy is the significant overestimation of the c cell parameter but this larger interlayer space does not affect the interatomic bond lengths that are only 1% larger than their experimental counterparts. It is well known that standard DFT does not capture accurately van der Waals interactions that govern the cohesion of talc layers. However, Larentzos et al. (2007) already demonstrated that first-principles calculations using DFT-GGA functionals are sufficiently accurate in predicting the mineral structure and vibrational properties of talc.

In the solid solution of interest, Mg atoms are progressively substituted by Ni atoms in octahedral sites. Because the ionic radius of Ni²⁺ (69 pm) is slightly smaller than the one of Mg²⁺ (72 pm), we obtain a mean Ni-O bond length (2.07 Å in the Ni100 model) slightly shorter than the mean Mg-O bond length (2.09 Å in the Ni0 model). This decrease is in

agreement with the values derived experimentally (2.055 Å for the Ni-talc according to the EXAFS analysis of Dumas et al. 2015, and 2.071 Å for the Mg-talc according to Rietveld refinement of X-ray diffraction patterns on large Mg natural talc single crystal of Perdikatsis and Burzlaff 1981). Thus the Mg-Ni substitution leads to a slight contraction of the crystal lattice. Cell parameters *a* and *b* decrease from 5.35 Å to 5.33 Å, and from 9.27 Å to 9.24 Å, respectively (Fig. 1).

3.2 Infrared spectra of Mg-talc and Ni-talc

Experimental infrared spectra of Mg-talc (sample Ni0) and Ni-talc (sample Ni100) are shown in Figure 2. The higher degree of crystallinity of Ni-talc already mentioned from the X-ray diffraction patterns is also visible in infrared spectroscopy. Absorption bands are sharper in Ni-talc. Above 3000 cm⁻¹, spectra are characterized by a broad band with its maximum at 3438 cm⁻¹ and a sharp band at higher frequency (3677 cm⁻¹ in Mg-talc and 3627 cm⁻¹ in Ni-talc). Below 1200 cm⁻¹, we can observe three groups of absorption bands at about 1000, 700 and 450 cm⁻¹. The striking difference between the spectra of Mg-talc and Ni-talc is in the group of bands around 700 cm⁻¹. Mg-talc displays a unique band at 670 cm⁻¹ while Ni-talc shows two bands at 668 cm⁻¹ and 710 cm⁻¹.

Infrared spectra have also been computed from first-principles calculations on models Ni0 and Ni100, taking into account the shape of talc particles. Indeed, for particles smaller than the infrared wavelength (sub-micron particles), the electric field (depolarization field) induced by surface charges in the polarized particles shifts the absorption bands and affects their intensity with respect to the resonances of the dielectric tensor of the bulk mineral (e.g., Balan et al. 2008a). These resonances of the dielectric tensor correspond to the spectra at the bottom of Figure 2. Three particle shapes have been considered: a plate perpendicular to the *c** axis, a sphere and an intermediate shape (oblate spheroid). The correspondence between

theoretical and experimental absorption bands is straightforward (Fig. 2). For Mg-talc, the plate shape provides the best description of the bands observed at 670, 538 and 450 cm^{-1} , and in particular their spacings. For Ni-talc, only the plate shape gives the right ratio of intensity between the two bands at 668 and 710 cm^{-1} and in the same time, the intense and rather symmetric band at 1030 cm^{-1} . This suggests that the particles of the synthetic sub-micron talc samples reflect their layered structure and probably have only few talc sheets. A large stacking of talc sheets relative to the lateral extension of the particle would approach the sphere model instead.

Looking at the theoretical vibrational modes enables us to assign the observed absorption bands. The sharp band above 3600 cm^{-1} corresponds to the stretching vibration of the structural OH groups. The difference in wavenumber between calculated and observed OH bands is at least partly explained by the anharmonicity. OH stretching vibrations show a certain degree of anharmonicity while calculations are performed within the harmonic approximation. The broad band around 3438 cm^{-1} is not related to the talc structure. It is usually assigned to weakly bound water and will be discussed further. The normal mode calculated at about 900 cm^{-1} (bottom spectrum of Fig. 2) corresponds to a Si-O stretching mode polarized along the c^* axis while the more intense band calculated at $\sim 980 \text{ cm}^{-1}$ is due to two degenerated Si-O stretching modes polarized in the (ab) plane. For the plate shape, the band at $\sim 980 \text{ cm}^{-1}$ remains at the same position while the band at $\sim 900 \text{ cm}^{-1}$ shifts to higher wavenumbers. The two bands become superimposed in Ni-talc, which contributes to the strong intensity and symmetry of the band observed at 1030 cm^{-1} . While in Mg-talc, the mode polarized along the c^* axis appears at even higher wavenumber than the modes polarized in the (ab) plane, thus explaining the asymmetric shape of the band observed at 1018 cm^{-1} with a shoulder at $\sim 1060 \text{ cm}^{-1}$. At lower wavenumber, the band at 670 cm^{-1} in Mg-talc and 710 cm^{-1} in Ni-talc corresponds to OH libration motions. Our analysis of the theoretical data also

shows that in Ni-talc, even if the band observed at 668 cm^{-1} appears in the same region, the vibrational mode involved is fundamentally different. This band corresponds to a lattice mode polarized along the c^* axis and involving Ni, O and H atoms. In Mg-talc, the same mode (involving now Mg, O, H atoms) gives rise to the band observed at 538 cm^{-1} . Finally, the most intense doublet at $\sim 450, 467\text{ cm}^{-1}$ is assigned to lattice modes polarized in the (ab) plane and involving all atoms.

3.3 Infrared spectra of OH stretching bands in the Mg-Ni series

Figure 3 reports the measured near-infrared and mid-infrared spectra in the range of the first overtones and fundamentals OH stretching modes for the five synthetic samples. Both spectra look very similar with the presence of up to four main absorption bands. The decomposition of all spectra required considering, in addition to these four bands, two less intense contributions on the high frequency side (at 7226 and 7206 cm^{-1} for the first overtones, and at 3716 and 3687 cm^{-1} for the fundamental modes). These contributions were assigned to OH groups on sheet edges by Dumas et al. (2013c). The spectra decompositions can be found in supplementary information (Figs. S2 and S3), and the derived data for the four main OH bands are compiled in Table 3. These absorption bands remain nearly at the same wavenumbers over the entire solid solution (at $3677, 3662, 3646$ and 3627 cm^{-1} for the fundamental modes). However, as reported by Wilkins and Ito (1967) for well-crystallized synthetic samples, a closer look indicates that the separation between bands slightly decreases when Ni content increases. This variation does not exceed 3 cm^{-1} over the entire compositional range. It is possible to assess the anharmonicity of OH vibrations from the wavenumbers of fundamental modes ($W_{\nu OH}$) and first-overtones ($W_{2\nu OH}$), by calculating the anharmonicity constant, $X = W_{2\nu OH}/2 - W_{\nu OH}$ (Bourdron and Sandorfy 1973). Results are given in Table 3. Considering the standard deviations, we found the anharmonicity constant to

be the same for all OH stretching modes and for all compositions, $X = -85.0 \pm 2.2 \text{ cm}^{-1}$ (2σ). It is in good agreement with the value found by Petit et al. (2004b) for various natural and synthetic talcs, $X = -86.0 \pm 2.5 \text{ cm}^{-1}$. The anharmonicity constant being independent on the clay chemistry, these authors could apply this relation in order to improve the interpretation of the near-infrared spectra of other phyllosilicates like smectite and kaolinite polymorphs.

Figure 3 also shows the theoretical spectra obtained for the talc models considered. Talc unit cell contains six octahedral sites (2 M1 sites and 4 M2 sites). For the Ni17 model, one Ni atom was placed in either M1 or M2 site. The two spectra are equivalent. In a similar manner, the Ni83 model corresponds to one Mg atom placed in either M1 or M2 site, which leads to the same spectrum. For the Ni50 model, several configurations of the three Ni atoms over the six octahedral sites have been tested, and the two spectra obtained are shown in Figure 3. Theoretical spectra, like measured ones, display up to four absorption bands. We can already note that the distribution of the cations on the octahedral sites affects significantly the infrared spectrum (number of bands and their intensities). For a given composition, the limited size of the simulation cell imposes an ordered cation distribution that does not reflect the distribution occurring in synthetic or natural samples. This explains the differences observed between experimental and theoretical spectra in figure 3. Wavenumbers and absorbances derived from the theoretical spectra are listed in Table 4. Talc unit cell contains four hydroxyl groups. Due to their position perpendicular to the layers, all OH stretching modes are polarized along the c^* axis. Each hydroxyl group is bonded to three octahedral cations. In order to know which hydroxyl group is involved in each vibrational mode, we calculated the displacement of each of these four H atoms (Table 4). Results confirm unambiguously the assignment of the four main absorption bands. From high to low frequency, the four bands correspond to the stretching vibration of hydroxyl groups bonded to 3Mg, 2Mg1Ni, 1Mg2Ni, and 3Ni atoms. The present data also demonstrate that there is no

coupling between hydroxyl groups with distinct cationic environments. These conclusions fully support the interpretation of Wilkins and Ito (1967).

3.4 Water adsorption on edge sites

Natural talc is known to be hydrophobic in relation with its sheet-like morphology of few tens of micrometers wide (Fig. 4). Indeed the very large basal hydrophobic surface dominates over the lateral surfaces (sheet edges), which display however many reactive sites and a hydrophilic behavior. Talc particles synthesized here conserve their sheet-like morphology but present sub-micron sizes. As illustrated in figure 4, the particles size decreases drastically and concomitantly the proportion of sheet edges increases making the hydrophilic behavior measurable. This is clearly evidenced by thermogravimetric analyses (Dumas et al. 2013c). While natural talc has a single loss of weight around 950 °C corresponding to its destabilization, synthetic sub-micron talc undertakes two additional losses before 150 and 450 °C, attributed first to physisorbed water and second to silanols (Si-OH) and magnesium hydroxides (Mg-OH) on the sheet edges. This previous study employed spectroscopic techniques (nuclear magnetic resonance and infrared spectroscopies) to access the edges contributions of synthetic sub-micron Mg-talc. In ¹H NMR spectra, two new narrow and distinct peaks were interpreted as associated to physisorbed water and silanol groups. In near-infrared spectra, two small contributions at 7200 and 7230 cm⁻¹ (next to the band at 7185 cm⁻¹ of structural OH groups) were assigned to OH groups on edge sites, i.e. Si-OH and Mg-OH respectively. In order to investigate further the influence of sheet edges on the infrared spectra, we built surface models with several distinct hydroxyl groups (OH bonded to one Si, to one Si and one Mg, or to two Mg) and water molecules chemisorbed on a Mg site (Fig. 5). These models do not consider physisorbed water molecules.

During the structural optimization of both surfaces (100) and (010) of Ni-talc, a water molecule desorbed. This molecule was removed before calculating the vibrational properties. Therefore the surface relaxation differs between Ni-talc and Mg-talc. The final arrangement of hydroxyl groups is different. Results analysis indicates that hydroxyl groups pointing outward vibrate at a frequency close to the structural hydroxyl groups. On the contrary, Si-OH groups pointing toward another talc layer or OH groups pointing toward another O atom of the sheet edge vibrate at lower frequency. The stronger the hydrogen bond formed, the lower the frequency of the associated absorption band. These results suggest that the observed broad band centered at 3440 cm^{-1} is due not only to the physisorbed water molecules (not modeled here) but also to the multitude of geometries of hydroxyls chemically adsorbed on edge sites. In experimental studies investigating the infrared absorption bands related to structural OH groups, the spectrum baseline is defined in such a way that the contribution of the broad band is removed but small features remain on the high-frequency side. As mentioned above, Dumas et al. (2013c) looked at these small bands in the near-infrared region for synthetic Mg-talc. Above the structural OH band (7185 cm^{-1}), the two weak bands at 7200 and 7230 cm^{-1} were assigned to Si-OH and Mg-OH respectively. It is worth mentioning that, in the mid-infrared region, our calculations lead to similar features. Above the structural OH band calculated at 3848 cm^{-1} , we found two weak bands at 3873 and 3885 cm^{-1} related to Si-OH and $\text{Mg}_2\text{-OH}$ groups respectively.

3.5 Quantification of the chemical composition

The four main OH stretching bands are now unambiguously attributed to specific structural OH groups defined by their cationic environment. For the mid-infrared region, the bands at 3677 , 3662 , 3646 and 3627 cm^{-1} are related to hydroxyl groups bonded to 3Mg , $2\text{Mg}1\text{Ni}$, $1\text{Mg}2\text{Ni}$, 3Ni atoms, respectively. In order to use the relative absorbance of these

bands (i.e. ratio of bands areas) to quantify the concentration of each of the hydroxyl types and therefore the chemical composition of the talc, one has to assume that the absorption coefficients of these different hydroxyls are the same whatever the local chemistry around OH groups. This is generally assumed in most experimental studies (e.g., Petit et al. 2004a). However it has been shown (Balan et al. 2008b) that considering many minerals, absorption coefficients of OH stretching modes globally decrease with increasing frequency. This assumption of constant absorption coefficients can be checked from our theoretical study.

Theoretical molar absorption coefficients, K_{int} , and the relative integrated absorbances for each vibrational mode (i.e. each OH band) are given in Table 4. We can note that with a mean value of $K_{int} = 9071 \text{ Lmol}^{-1}\text{cm}^{-2}$, the talc OH groups have an absorption coefficient similar as inner OH groups of lizardite and clinocllore (Balan et al. 2008b). Most importantly, if we look at the relative absorbance of each OH band for a given sample, we see variations, but these variations do not follow systematic trends. In model Ni17, both bands contribute almost equally to the total absorbance. In model Ni50a, bands with lower wavenumbers contribute slightly more (up to 26.8%) than bands with higher wavenumbers (down to 22.4%). But this trend is opposite in model Ni83. We can consider these variations either as inherent to the configurations investigated or due to the uncertainty of the calculation (absorption coefficients are properties extremely sensitive to the structural optimization). To clarify this point, we estimate the composition of these fully constrained models from these values of relative absorbance. Table 5 shows for instance for the model Ni50a, that the calculated relative absorbances lead to a composition of 52.5 mol % Ni, different from the expected 50 mol % Ni that one obtains if OH band contributes equally to the total absorbance. The present theoretical results suggest that the small observed variations are related to computational uncertainties and therefore that the assumption of a constant absorption coefficient whatever the cationic environment around the hydroxyls is correct.

The procedure is applied to the synthetic samples and talc compositions obtained from the relative integrated absorbances of either the fundamental modes or the first-overtone modes are compared (Table 6). Assuming that during the synthesis process, all nickel is incorporated into the talc particles, we find that results from the near-infrared region are sensibly better than those from the mid-infrared region. They provide the correct composition within 2 mol %. Only sample Ni100 shows a larger difference of 6 mol % between the expected composition and the one derived from infrared spectroscopy. While no magnesium is used in the synthesis of this sample, both near- and mid-infrared spectra display a weak band (at 7123 cm^{-1} and 3646 cm^{-1} respectively), which could be attributed, according to its position, to OH groups bonded to one Mg and two Ni atoms. Note that Dumas et al. (2015) already reported the presence of such weak band for the Ni end-member of a similar synthetic sub-micron talc. The presence of this weak band either reflects a contamination during the synthesis or a wrong assignment. An electron microprobe analysis was performed on this Ni100 sample and leads to a Ni proportion of 98.8 ± 0.2 mol %, incompatible with the 94 mol % derived from infrared spectroscopy. Therefore the weak band at 7123 cm^{-1} cannot be explained by a Mg contamination. As suggested by the calculated spectra of surface models for Ni-talc (Fig. 5), this weak band is rather related to OH groups on edge sites, like Ni-OH or Si-OH. This assignment is also supported by the fact that a band located at a similar wavenumber (7121 cm^{-1}) was previously observed by Christy (2010) on a silica gel surface.

3.6 Cationic distribution

The infrared spectroscopic data can also be used to discuss the distribution of cations in the octahedral sheet (Petit et al. 2004a). If Mg and Ni atoms are randomly distributed, the four OH bands should occur with the probabilities specified in Table 7. It is therefore possible to calculate the relative integrated absorbances that one expects for a given composition and a

random distribution of octahedral cations. These values are compared with the relative absorbances obtained by spectral decomposition in Table 7 and Figure 6. The good correlation observed in Figure 6 indicates that divalent cations are randomly distributed in the octahedral sheets of these synthetic sub-micron talc samples like in the various natural samples investigated by Petit et al. (2004a). This conclusion is supported by our DFT calculations, which predict that nickel has no preference for M1 and M2 octahedral sites. The energy difference (0.3 kJ/mol) is one order of magnitude smaller than the thermal energy at ambient temperature.

4. Conclusion

This combined experimental and theoretical infrared spectroscopic study allowed us to characterize further a synthetic talc product with potential industrial applications. Over the whole range of the Mg-Ni solid solution, the sub-micron talc particles present: (i) a random distribution of Mg and Ni cations in the octahedral sheets, (ii) platy shapes nicely reflecting their layered structure, and (iii) an interesting hydrophilic character related to the large proportion of sheet edges. The Mg-Ni substitution is also accompanied by an increase in the crystallinity degree.

The confrontation of measured and calculated infrared spectra enabled to fix the spectra interpretation to firm physical basis. Absorption bands below 1200 cm^{-1} have been assigned to the corresponding vibrational modes, allowing us to understand the differences observed between Mg-talc and Ni-talc. In the OH stretching region related to structural hydroxyl groups, our calculations show no coupling between the stretching modes of OH groups distinguishable by their cationic environment. Results thus fully support the

assignment made by Wilkins and Ito (1967). We have also demonstrated that absorption coefficients of OH groups are constant whatever the cationic environment of these hydroxyls. This validates the key assumption for quantifying the talc composition from the relative absorbance of OH bands.

The surface models considered here suggest that the infrared signatures of hydroxyls adsorbed on the reactive sites of sheet edges fall in the same wavenumber range as the broad band assigned to physisorbed water molecules (band observed between 3000 and 3700 cm^{-1}). In more details, the bands related to the most weakly hydrogen-bonded OH surface groups are located in the same range as the bands attributed to OH structural groups. This observation might hinder the accurate determination of talc composition. However absorption bands related to OH surface groups have relatively weak intensities and do not affect the infrared-derived composition by more than a few percent.

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506 Table 1: Starting materials used for the preparation of talc precursors.

Sample	sodium metasilicate pentahydrate	magnesium acetate tetrahydrate	nickel acetate tetrahydrate	acetic acid	sodium acetate trihydrate
Ni0	0.10 mol	0.075 mol	0.000 mol	50.0 ml	50.0 g
Ni25	0.10 mol	0.056 mol	0.019 mol	50.0 ml	50.0 g
Ni50	0.10 mol	0.038 mol	0.038 mol	50.0 ml	50.0 g
Ni75	0.10 mol	0.019 mol	0.056 mol	50.0 ml	50.0 g
Ni100	0.10 mol	0.000 mol	0.075 mol	50.0 ml	50.0 g

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511 Table 2: Calculated (this study) and experimental (Perdikatsis and Burzlaff 1981) cell
512 parameters and mean bond lengths of Mg-talc.

	Calc.	Exp.
<i>a</i> (Å)	5.349	5.290
<i>b</i> (Å)	9.268	9.173
<i>c</i> (Å)	10.116	9.460
α (°)	90.35	90.46
β (°)	98.28	98.68
γ (°)	90.01	90.09
Si-O (Å)	1.642	1.623
Mg-O (Å)	2.090	2.071
O-H (Å)	0.977	-

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Table 3: Infrared-active OH stretching modes of Mg-Ni talc samples: wavenumber (W in cm^{-1}) and relative integrated absorbance (A) for the fundamental (νOH) and first overtone bands ($2\nu\text{OH}$), anharmonicity constant calculated as follow $X = W_{2\nu\text{OH}}/2 - W_{\nu\text{OH}}$ (Bourdéron and Sandorfy 1973). Data derived from the spectra decomposition shown in supplementary information (Figs S2 and S3).

Sample	$W_{\nu\text{OH}}$	$A_{\nu\text{OH}}$	$W_{2\nu\text{OH}}$	$A_{2\nu\text{OH}}$	X
Ni0	3677	1.00	7184	1.00	-85
Ni25	3676	0.52	7184	0.43	-84
	3662	0.33	7154	0.35	-85
	3646	0.15	7119	0.19	-86.5
	-	-	7077	0.03	-
	3676	0.17	7185	0.18	-83.5
Ni50	3662	0.41	7156	0.34	-84
	3646	0.33	7121	0.34	-85.5
	3625	0.10	7078	0.14	-86
	3676	0.03	7183	0.05	-84.5
	3662	0.25	7157	0.14	-83.5
Ni75	3647	0.43	7122	0.30	-86
	3625	0.28	7079	0.51	-85.5
	3646	0.20	7123	0.17	-84.5
	3627	0.80	7080	0.83	-87

538 Table 4: Theoretical infrared-active OH stretching modes of talc models: wavenumber (W in
539 cm^{-1}), normalized displacement (a.u.) of each of the four H atoms of the simulation cell
540 defined by their cationic environment, integrated molar absorption coefficient (K_{int} in Lmol^{-1}
541 cm^{-2}) and contribution of each mode to the total absorbance (%).

Model	W	Norm. displ. and neighbor cations				K_{int}
Ni0	3848	3Mg	3Mg	3Mg	3Mg	8117
		0.49	0.49	0.48	0.48	100%
Ni17	3849 3826	3Mg	3Mg	2Mg1Ni	2Mg1Ni	8958
		0.69	0.69	0.03	0.03	49.7%
		0.03	0.03	0.69	0.69	50.3%
Ni50a	3851 3828 3799 3762	3Mg	2Mg1Ni	1Mg2Ni	3Ni	9327
		0.97	0.02	0.01	0.01	22.4%
		0.02	0.97	0.02	0.01	24.5%
		0.01	0.02	0.97	0.01	26.3%
		0.01	0.01	0.01	0.97	26.8%
Ni50b	3827 3797	2Mg1Ni	2Mg1Ni	1Mg2Ni	1Mg2Ni	9778
		0.81	0.53	0.01	0.01	47.5%
		0.01	0.01	0.74	0.63	52.5%
Ni83	3800 3762	1Mg2Ni	1Mg2Ni	3Ni	3Ni	9377
		0.69	0.69	0.01	0.01	52.6%
		0.01	0.01	0.69	0.69	47.4%
Ni100	3765	3Ni	3Ni	3Ni	3Ni	8868
		0.49	0.49	0.48	0.48	100%

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544 Table 5: Ni proportions in theoretical models estimated from the relative integrated
545 absorbances and compared to the exact value.

Model	mol % Ni from A	Exact mol % Ni
Ni17	16.77	16.67
Ni50a	52.50	50.00
Ni50b	50.83	50.00
Ni83	82.47	83.33

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548 Table 6: Ni proportions in synthetic samples estimated from the relative integrated absorbances of the fundamental and first overtone OH bands.

Sample	mol % Ni from ν OH	mol % Ni from 2ν OH
Ni0	0	0
Ni25	21	27
Ni50	45	48
Ni75	66	75
Ni100	93	94

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551 Table 7: Relative integrated absorbances for the fundamental (ν OH) and first overtone (2ν OH) OH bands, calculated assuming a random
552 distribution of octahedral cations (rand). In that case, we used the sample composition derived from infrared spectroscopy and the probabilities of
553 occurrence of each OH band that are specified in the Table. Results are compared to the ones obtained by spectral decomposition (dec).

OH group	Probability	Ni25 ν OH		Ni25 2ν OH		Ni50 ν OH		Ni50 2ν OH		Ni75 ν OH		Ni75 2ν OH		Ni100 ν OH		Ni100 2ν OH	
		rand	dec	rand	dec	rand	dec	rand	dec	rand	dec	rand	dec	rand	dec	rand	dec
Mg ₃ OH	[Mg] ³	0.49	0.52	0.39	0.43	0.17	0.17	0.14	0.18	0.04	0.03	0.01	0.05	0.00	0.00	0.00	0.00
Mg ₂ NiOH	3[Mg] ² [Ni]	0.39	0.33	0.43	0.35	0.41	0.41	0.39	0.34	0.23	0.25	0.14	0.14	0.01	0.00	0.01	0.00
MgNi ₂ OH	3[Mg][Ni] ²	0.10	0.15	0.16	0.19	0.33	0.33	0.36	0.34	0.44	0.43	0.42	0.30	0.18	0.20	0.15	0.17
Ni ₃ OH	[Ni] ³	0.01	0.00	0.02	0.03	0.09	0.10	0.11	0.14	0.29	0.28	0.43	0.51	0.81	0.80	0.84	0.83

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Figure captions

Figure 1: DFT optimized cell parameters of talc as a function of the Ni molar concentration. Angles ($\alpha = 90.35^\circ$, $\beta = 98.28^\circ$, $\gamma = 90.01^\circ$) remain nearly constant over the Mg-Ni series.

Figure 2: Experimental (top) and theoretical mid-IR absorption spectra of Mg-talc (sample and model Ni0) and Ni-talc (sample and model Ni100). Spectra have been computed for three particle shapes: a plate perpendicular to the c^* axis, a sphere and an intermediate shape. The trace of the imaginary part of the dielectric tensor computed for an infinite crystal (bottom) serves as reference and indicates the frequency of normal modes in absence of the depolarization field occurring in small particles.

Figure 3: Experimental IR spectra of Mg-Ni synthetic talcs (in the regions of fundamental modes and first overtones of OH stretching vibrations) compared to theoretical spectra of fundamental modes. Vertical dashed lines are guides for the eye.

Figure 4: Scanning electron microscope images taken at the same scale of a natural talc (A) and a talc synthesized using the present protocol (B) (images from F. Martin's library). C. Schematic representation of a talc particle (left) and the same particle split in four (right), highlighting that the basal surface remains constant in both cases while lateral surfaces are doubled. This explains why the hydrophilic character of talc increases when the size of talc particles decreases.

Figure 5: Structural models of the (100) and (010) surfaces of Mg-talc (left) and Ni-talc (right), with the corresponding theoretical IR spectra of OH and H₂O groups. Experimental IR spectra in the 4000 – 2700 cm⁻¹ range are shown for comparison (top).

581

582 Figure 6: Comparison of relative integrated absorbances calculated assuming a random
583 distribution of octahedral cations and obtained by spectral decomposition. Solid and open
584 symbols correspond to fundamental and first overtone OH bands, respectively.

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587 Figure 1:

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Electronic Supplementary Material
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