Sub-THz complex dielectric constants of montmorillonite clay thin samples with Na\textsuperscript{+}/Ca\textsuperscript{++}-ions

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We implement a technique to characterize electromagnetic properties at frequencies 100 to 165 GHz (3 cm\textsuperscript{-1} to 4.95 cm\textsuperscript{-1}) of oriented montmorillonite samples using an open cavity resonator connected to a sub-millimeter wave VNA (Vector Network Analyzer). We measured dielectric constants perpendicular to the bedding plane on oriented Na\textsuperscript{+} and Ca\textsuperscript{++}-ion stabilized montmorillonite samples deposited on a glass slide at ambient laboratory conditions (room temperature and room light). The clay layer is much thinner (∼30 µm) than the glass substrate (∼2.18 mm). The real part of dielectric constant, \(\epsilon_{re}\), is essentially constant over this frequency range but is larger in Na\textsuperscript{+} than in Ca\textsuperscript{++}-ioned clay. The total electrical conductivity (associated with the imaginary part of dielectric constant, \(\epsilon_{im}\)) of both samples increases monotonically at lower frequencies (<110 GHz), but shows rapid increase for Na\textsuperscript{+} ions in the regime >110 GHz. The dispersion of the samples display a dependence on the ionic strength in the clay interlayers, i.e., \(\zeta\)-potential in the Stern layers.
I. INTRODUCTION

Clay minerals have a complex layered structure with exchangeable cations that can bind water molecules in the inter layers. With increasing pressure and temperature, or in the presence of polar free radicals, these interlayer cations can be exchanged. This cation exchange capacity (CEC) of clay minerals affects their fluid conductivity and permeability; dielectric permittivity. Complex dielectric properties of clay are crucial to determine hydrocarbon-contents in oil-rich rocks. These measurements are usually performed at logging frequencies in the kHz-range and between 0.5 MHz and 1.1 GHz. Complex conductivity of clayey materials between 1 mHz and 45 kHz for CEC effects was characterized and modeled. Canan researched dielectric properties of montmorillonite clay samples in detail, explaining interlayer polarization and relaxation mechanisms between 30 kHz-300 MHz. Some clay minerals can swell due to hydration with water adsorbed in the interlayer depends on the charge of the interlayer cations. Electrical measurements can yield cation mobility. Dielectric measurements can be instrumental to characterize the water absorbed in montmorillonites. The conductivities of montmorillonite clay saturated by mono valent cations was studied where Debye and Maxwell-Wagner relaxations are discussed in details. These frequency- and temperature-dependent measurements were in the frequency range between 300 and 10,000 Hz, and from -150°C to +30°C. THz dielectric constants of layered silicates including muscovite, vermiculite, phlogopite, and biotite, have been measured by THz-time domain (THz-TDS) spectroscopy. In this paper we look at Montmorillonite using much higher resolution CW methods based on harmonic multiplication of phase stabilized microwaves, electronically generated; these methods provide very low noise/high dynamic range out to about 1.4 THz at present.

At CSM We use 3 millimeter wave (or sub-THz) modalities: (1) A Quasi Optical System to study bulk properties, (2) A Near Field Scanning System to measure local properties, and (3) the Open Hemispherical Cavity Resonator for samples that are too optically thin or low loss for quasi-optical techniques. Using cavity resonance we measure these complex dielectric constants of clay-thin films in 100-165 GHz or 0.1-0.16 THz and investigate electrical properties in the presence of Ca²⁺/Na⁺-ions. We study how these cations influence conductivity of free carriers, and relaxations. We also compare our data with the low frequency measurements.
II. METHODS

We use an open hemispherical open cavity resonator with VNA (Vector Network Analyzer) to measure electrical properties of thin sections of clay-samples with Ca$^{++}$/Na$^{+}$-ions infused. The cavity is a structure with two copper mirrors positioned at certain distance (the “cavity length”) without any sidewalls. The top mirror is hemispherical and connected to two WR-10 waveguide couplers working as a transmitter and a receiver, and on the other hand the lower mirror is flat and smaller than the upper one in size. We measured the real part of refractive index of $\sim 1$ mm-thick glass substrate (borosillicate) to be 1.98 at 310 GHz which is the same as its theoretical value. For details on the cavity and methodology see Rahman et al.

A. Open Cavity Resonator

The principle of this technique is cavity perturbation. The changes in axissymmetric (00q) mode profiles, mainly the frequency-shift and linewidth-variation, between an empty cavity mode and the same mode in presence of a sample, determine the complex dielectric constant of the sample. The unloaded (empty) cavity has an axisymmetric mode spacing that is $c/2L$, where L is the distance between two mirrors, also known as cavity length. In our cavity, since L is around 15 cm, the unloaded mode spacing is about 1GHz.

Putting a sample on the bottom mirror perturbs the modes in a calculable but nontrivial way. To avoid geometrical factors, we do a second perturbation which involves flipping the sample upside down. Since the boundary values of the E-field are different, we are able to get a simple (geometry-free) formula for the complex permittivity from 3 sweeps around a 00q mode.

This complex dielectric permittivity is related to total electrical/optical conductivity and absorption coefficient with the use of basic theory of electromagnetism as

\[ n_{re}\alpha = 120\pi\sigma_{re} = 30\omega\epsilon_{im} \]

Where $n_{re}$ and $\sigma_{re}$ are the real part of the refractive index and conductivity (in $\Omega^{-1}\text{cm}^{-1}$), $\epsilon_{im}$ is imaginary part of the complex dielectric constant, and $\omega$ and $\alpha$ are labeled for frequency and absorption coefficient, both of them are in wave numbers ($\text{cm}^{-1}$), where $1\text{cm}^{-1} = 30$ GHz. The conductivity is a macroscopic quantity which can be optical, electronic or
FIG. 1. Perturbations with substrate only, film up, and film down set-ups for clay with (a) Ca\textsuperscript{++} and (b) Na\textsuperscript{+} ions (at room temperature).

ionic depending on the system and the frequency range of the probe. This is also valid for absorption coefficient. These parameters, $\sigma_{re}$ and $\alpha$, essentially describe the loss mechanisms in a material.

### B. Measurements

By sweeping the VNA, we identified the axissymmetric empty cavity modes based on constant frequency-spacing. This fixes the cavity-length, $l$, to be 145.56 mm and kept it unchanged throughout the experiments. We measured the eigenfrequency-shifts and modal quality factors (Q-values related to a linewidth) for substrate-only, film up and film down positions in order to apply the differential method. In order to determine uncertainty in the experiment, we repeat the entire procedure of inserting the sample, performing the measurements, and taking it out for six times and calculating the variations in frequency shifts and linewidth changes of substrate. In cavity paper,\textsuperscript{14} we showed that by re-doing the entire procedure for six times for borosillicate glass substrate, we obtained standard deviations $<1.0\%$ in measuring its complex dielectric constant. This uncertainty can also propagate to the calculations of dielectric constant. We confirmed during each trial, the same part of the samples is probed to make it consistent.

The frequency shifts due to film up, film down, and substrate only are used in the Eqs.(1)
for flipflop method, to determine the real part of the refractive index of a thin film.\(^{15,16}\)

\[
\frac{\delta \nu_f}{\delta \nu_s} = \frac{n_f^2 - 1}{n_s^2 - 1}.
\]

(1)

With

\[
\delta \nu_f = \nu_{(fup)} - \nu_{(s)}.
\]

(2)

\[
\delta \nu_s = \nu_{(fdown)} - \nu_{(s)}.
\]

(3)

Where, \(\nu_{(fup)}\), \(\nu_{(fdown)}\) and \(\nu_{(s)}\) represent the eigenfrequency associated with the film on the top (film up), film at the bottom (film down), and the substrate only, respectively. The term, \(\delta \nu_s\), stand for the difference between the eigenfrequencies associated with film at the bottom of the substrate and the substrate only, and the term, \(\delta \nu_f\), is the difference between the eigenfrequencies with the film at the top of substrate and the substrate only. The required condition is the real part of the refractive index of substrate must be known. The real of part of the dielectric constant of thin film can obtained by \(\epsilon_{re}^{(f)} = (n_{re}^{(f)})^2\). We need Q-values of film up and substrate (only) to calculate the imaginary part of complex dielectric constant of the thin film. The Q-value of a resonant peak (perturbation) is defined as \(Q = \nu_0 / \Delta \nu\). The Q-value is related to the imaginary part of the refractive index by \(n_{im}^{(f)} = 1/2Q\). In the fipflop method, \(Q^{(f)} = (Q^{(filmup)} - Q^{(substrate)})\). Now, we are able to compute the imaginary of the complex dielectric constant of the thin film by \(\epsilon_{im}^{(f)} = 2n_{re}^{(f)} n_{im}^{(f)}\).

C. Samples and Sample preparations

We studied montmorillonite clay minerals from Clay Mineral Society that were treated to yield homoionic, univalent (Na\(^+\)) and divalent (Ca\(^{++}\)) samples. The samples were treated to remove carbonate and iron oxide cements with a Na-acetate buffer and Na-dithionite respectively.\(^{21}\) The sub-0.5 \(\mu m\) equivalent spherical diameter size fractions were separated from samples by standard centrifugation methods. Then the Na\(^+\) saturated clay was thoroughly cleaned with dialysis to remove excess salt. To prepare the Ca\(^{++}\) exchanged smectite, a dialyzed Na\(^+\) sample was treated with a 1M solution of CaCl\(_2\), and shaken for at least two hours, excess solution was decanted and the process was repeated twice more. The excess Ca\(^{++}\) salt was removed with dialysis.\(^{22}\) Oriented aggregates were made by evaporation onto glass slides to provide a sample \(\sim 4\) cm long with at least 10 mg clay per cm\(^2\).\(^{22}\)
In addition to millimeter wave EM analysis, we performed a variety of measurements on the samples, including thermal gravimetric analysis (TGA), subcritical Nitrogen gas adsorption (SGA) and X-ray diffraction (XRD) on oriented samples.

TGA experiments were performed using a TA Instruments Q5000 purged with dry filtered reagent grade nitrogen. Prior to the analysis, the samples were equilibrated at ambient conditions (50% RH). Approximately 25 mg of each sample was used for the experiments. The weighing error is believed to be <0.001 mg. The heating rate for all cycles was fixed at 5 °C/min. The inert nitrogen purge gas flow rate was constant at 25 mL/min. DTG patterns reflecting reaction rates and relative hydration energy were obtained by taking the first derivative of the percent weight loss vs. temperature curves.

Specific surface area (SSA), and pore-size distribution (PSD), of the Na+ and Ca2+ smectite forms were measured using the subcritical nitrogen gas adsorption (SGA) at 77 K. About 1-2 g of sample was degassed by heating at 200 °C under vacuum (10 mmHg) until the out-gassing rates was <2 mmHg/min over a 15 min interval. Measurements in both adsorption and desorption mode were performed over the entire partial pressure range with average number of 85 measurement points. SSA for each sample was determined by inversion of the adsorption branch of the isotherm using a modified BET procedure23. Pore-size distribution (PSD) is obtained by inverting the adsorption branch of the isotherm using BarettJoynerHalenda (BJH) method assuming cylindrical nonconnecting pores24.

The sub 500 nm equivalent spherical diameter size fraction was separated from bulk material by standard centrifugation methods following treatment to remove carbonate and Fe-oxide cements with a Na-acetate buffer and Na-dithionite, respectively (Jackson 1985). A portion of the Na+ saturated clay was treated by dialysis to remove excess salt and retained, and a second portion was thoroughly exchanged with Ca2+, and also treated with dialysis to remove excess salt (McCarty et al., 2009).

Oriented aggregates were made by evaporation onto glass slides to provide a sample 4 cm long with at least 15 mg clay per cm2 (Moore and Reynolds 1997). Diffraction scans were collected with a Thermo Xtra diffractometer with a - goniometer and a 250 mm radius, equipped with a solid-state Si detector in the air-dried (AD) state, and after ethylene glycol (EG) treatment by vapor solvation in a heated chamber (60 C). The scans were made from 2 to 52 2 with a 0.02 2 step increment and counting rate of 4 s per step or longer using CuK radiation transmitted through a 1.00 mm divergence and 1.80 mm antiscatter slit. Detector
TABLE I. Dielectric parameters for clay samples with Na\(^+\) and Ca\(^{++}\)-ions from various sources:

(* indicates the data presented in this research paper)

(** mentions these values are normalized with water)

| Clay-Na\(^+\) | Clay-Ca\(^{++}\) | Frequency | Sources |
|---------------|-----------------|-----------|---------|
| \(\epsilon_{re}\) | \(\sigma_{re}^*(\Omega^{-1}\text{ m}^{-1})\) | \(\epsilon_{re}\) | \(\sigma_{re}^*(\Omega^{-1}\text{ m}^{-1})\) | (kHz/MHz/GHz) | (Data) |
| ~ 217 - 80    | ~ 0.009 - 0.055 | ~ 104 - 80 | ~ 0.0046 - 0.02 | 0.5 MHz -0.1 GHz | Raythatha et al.\(^{11}\) |
| 7.8           | 0.69 - 40.2     | 4.86      | 0.48 - 4.98    | 100 - 165 GHz    | Rahman et al.* |
| 5 - 6**       | 0.0015 - 0.00375** | 1 GHz   | Well logging\(^{33}\) |

slits were 2.00 and 0.3 mm. The dielectric analysis was performed on these oriented aggregate preparations.

Finally XRD patterns from the air-dried oriented aggregate smectite specimens in Ca\(^2+\) and Na\(^+\) forms were simulated to reveal the relative proportions of interlayer spacings corresponding to 2, 1, and 0 water layers of interlayer cation hydration\(^{25,28}\).

III. RESULTS AND DISCUSSION

The real part of the dielectric constants of both clay samples maintain (almost) constant values indicating that carrier concentrations are low in both\(^{29,30}\). The imaginary part of dielectric constant and electrical conductivity of Na\(^+\)-ionized one, increase at two different rate where the faster in the higher frequency range and slower at low frequencies. The faster rate represents a nonlinear increase. The presence of both Debye relaxation\(^{31}\), and Maxwell-Wagner relaxation\(^{32}\) at radio frequencies was reported\(^5\). But between 100 and 165 GHz, phonon induced-relaxation is dominant\(^{29}\).

Revil et al.\(^5\) proposed a theoretical model to study complex conductivity-dependences on cation excahange capacity (CEC), specific surface area (SSA), and salinity for clay samples at low frequency. This model also relates CEC to SSA area with consistency\(^5\). It is reported that SSA increases exponentially for Na\(^+\)-clay and linearly for Ca\(^{++}\)-clay sample\(^{33}\). From our research, it is evident that conductivity depends on CEC or SSA. The larger CEC or exponential-growing SSA can contribute to more disperse Stern layer and the smaller CEC or linearly-progressive SSA stabilize the Stern layer. Thus, electrical conductivity is linked
FIG. 2. High frequency (100-165 GHz) data of (a) real part and (b) imaginary part of the complex dielectric constants of clay samples with Na\(^+\)/Ca\(^{++}\)-ions (at room temperature); (c) conductivity of both samples (inner plot is the expansion of the 100-110GHz responses).

to CEC (Cation Exchange Capacity) and zeta potential in the Stern layer.\textsuperscript{11} The Na\(^+\) makes a thicker unstable double layer where these high mobility ion are able to polarize rapidly. Therefore, the conductivity is more dispersive. This interlayer polarization is correlated to relaxation mechanisms. The relaxation processes is, therefore, dependent of ζ-potential which is also correlated to CEC.\textsuperscript{35} On the other hand, The imaginary part of dielectric constant and conductivity of the sample with Ca\(^{++}\) increase monotonically and sublinearly. The Ca\(^{++}\) creates more stable double Stern layer. Due to low mobility, the interlayer polarization is less disperse so its conductivity is sublinear. Since, \(\epsilon_{im} = 2 \left(1/\nu\right) \sigma_{re}\), the effect of \(1/\nu\) is more into imaginary part of complex dielectric constant of samples with Na\(^{++}\) than that of Ca\(^{++}\). In this case, \(\epsilon_{im}\) at high frequencies faced steeper decrease than at lower frequency ends.

From Table (I), it is obvious that in the sub-THz, the conductivities of clay-Na\(^+\)/Ca\(^{++}\)-ions are almost 2 to 3 orders of magnitude higher than in the RF/microwave range; on the
contrary, the real part of dielectric constants for both samples, decrease by $\sim$ one order of magnitude. This illustrates clay sample with Na$^+$ may have multiple relaxations. These high $\sigma_{\text{re}}$ values (for both ions) indicate the electron polarization in the Stern layer involve with phonon-mediated interactions. The lower and constant values of $\epsilon_{\text{re}}$ also confirm that there are depletions of mobile charges due to phonon interactions causing the diffused layers to thin.

Finally we looked at the measured and simulated XRD patterns collected for the various samples (Figures 5, 6 and 7).
FIG. 4. Subcritical nitrogen gas adsorption (SGA) data at 77 K for the Ca$^{2+}$ (black points) and Na$^+$ (shaded points) forms of SWy smectite. (A) Adsorption and desorption isotherms with relative pressure (P/P₀) compared with quantity of adsorbed gas. (B) Pore size distribution of each sample, where pore diameter is compared to the volume of each size. Specific surface area, and degas temperature of each sample is shown in the legend (see text).
FIG. 5. X-ray diffraction patterns collected in the air-dried (AD) ambient state from oriented aggregate sample preparations comparing Ca2+ (black) and Na+ (shaded) smectite forms. Basal 00l reflection d-spacings are shown on the figure in angstrom units (1Å = 0.1 nm).

FIG. 6. Experimental (black) X-ray diffraction pattern collected in the air-dried (AD) state from the Ca2+ form oriented aggregate smectite sample preparation compared with the simulated diffraction pattern (shaded). The simulated diffraction pattern consists of 86% of smectite layers with 2 layers of water molecules having a d-spacing of 14.94 Å, and 14% of smectite layers having 1 layer of water molecules and a d-spacing of 12.80 Å(1Å = 0.1 nm).
FIG. 7. Experimental (black) X-ray diffraction pattern collected in the air-dried (AD) state from the Na\(^+\) form oriented aggregate smectite sample preparation compared with the simulated diffraction pattern (shaded). The simulated diffraction pattern consists of 93% of smectite layers with 1 layer of water molecules having a d-spacing of 12.52 Å, and 7% of smectite layers having 0 layers of water molecules and a d-spacing of 10.10 Å (1Å = 0.1 nm).
IV. CONCLUSION

We measured sub-THz complex dielectric properties of clay samples with Na$^+$/Ca$^{++}$, and compute their $\epsilon_{re}$ and $\sigma_{re}$. We illustrate the connections between electromagnetic parameters and components of surface chemistry such as CEC or SSA, $\zeta$-potential. This also enables us to study the clay content and free radicals in shales, and to investigate their CEC and $\zeta$-potential-dependences. In future, we will study more different ionized clay samples and broader frequency ranges to capture more complete frequency-dependences of $\epsilon_{re}$ and $\epsilon_{im}$. This will allow us to model computationally the dispersions of these parameters.

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