

Dielectric, thermal and structural studies of montmorillonite, nontronite and their intercalates

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The subject of this dissertation was the study of the dielectric, thermal and structural properties of two smectite group minerals: montmorillonite and nontronite, as well as their intercalates. Minerals of the smectite group have a layered structure, which is characterized by a 2:1 type. It means that a single package consists of two tetrahedral ($[\text{SiO}_4]^{4-}$) layers separated by one octahedral ($[\text{AlO}_2(\text{OH})_4]^{5-}$) layer. The packages have a negative charge, which is equalized by cations such as Na^+ , Li^+ , K^+ and Ca^{2+} . Electrostatic interaction between counterions and packages causes their organization into larger structures called particles. In the natural environment, between the mineral packages there are water molecules bound in the form of layers. The number of layers depends on the temperature and humidity conditions. Water molecules are bound in a process called swelling, accompanied by an expansion of the interpackage space (an increase in the interlayer distance, d_{001}). The swelling properties of minerals not only involve water but also other molecules, so-called intercalants, examples of which are ethylene glycol, glycerol, methylamine and its derivatives, formic acid, heterocyclic compounds, and even tetracycline.

In this dissertation, the Author decided to apply the swelling properties of smectites to obtain their modifications during the intercalation process. Two materials were used for this purpose: montmorillonite K-10 (MMT-Na) commercially available and nontronite (NNT-Ca) mined near Leśna in Lower Silesia region. Nontronite is isostructural with montmorillonite, but its layers are richer in Fe^{III} and Fe^{II} in comparison to montmorillonite whose octahedral layer coordination centers are mainly occupied by Al^{III} . The studied minerals differ in terms of the type of counterion, where the interpackage spaces of nontronite contain Ca^{2+} ions, while those of montmorillonite Na^+ . It has been found that both nontronite and montmorillonite completely lose their interlayer water upon heating them to a temperature of 200°C. The swelling ability (intercalation property) gradually decreases after exceeding the annealing temperature of 300°C for montmorillonite and 350°C for nontronite. The mineral dehydration process is easily reversible and to rehydrate them it is sufficient to mix them with water. It has been shown that the hydration process occurs very quickly and is

exothermic. The obtained results allowed for proposing an effective procedure for modifying smectites, which involves the preliminary removal of interlayer water through a heating process while maintaining the mineral structure, followed by intercalating guest molecules into the interpackage spaces. Various compounds such as formamide, *N*-methylformamide, *N,N*-dimethylformamide, *N*-ethylformamide, *N*-methylacetamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, and ethylene glycol have been used in the intercalation process. The selection of modifiers was not arbitrary, but rather carefully considered based on specific electrical parameters of intercalants molecules (large dipole moments), their optimal sizes, proton-donor and proton-acceptor properties. As a result, a database of intercalant molecules was obtained. Based on it, the influence of additional substituents (methyl, ethyl groups) on dielectric relaxation (on the example of formamide and acetamide derivatives) could be verified. Moreover, the influence of the geometry of the guest molecules (on the example of DMSO and DMF) and the lability of the intercalant (on the example of *N*-ethylformamide and ethylene glycol) on the parameters of the relaxation process was assessed. Nontronite and montmorillonite intercalates were characterized by XRD, SEM-EDS, TG-DTA, and elemental analysis. The results of the measurements allowed to verify whether the intercalation took place and to determine the percentage of guest molecules bound between mineral packages.

The electrical properties of the modified smectites were evaluated based on the results obtained from broadband dielectric spectroscopy measurements. The current study aimed to evaluate changes in the electrical properties of modified smectites by determining dielectric relaxation parameters (relaxation times, dielectric increments, broadness coefficients) and activation energies. In the thesis, one attempted to determine the role of both: counterions and guest molecules in the process of dielectric relaxation of minerals and their intercalates. The preliminary study was focused on determining the potential impact on the electric permittivity and relaxation processes of such factors as the form of the measured sample (powder, pellet), AC/DC voltage, and thermal treatment of the samples. Based on the preliminary results, it was found that both the pelletization and the DC voltage did not affect the relaxation in the frequency radio range. However, it was noticed that they significantly reduce low-frequency electric permittivity and conductivity, which leads to improvement of the shape of dielectric relaxation curves. In the example of nontronite intercalated with *N*-methylacetamide, it was demonstrated that pelletization does not affect the amount of intercalant bound in interpackage spaces. It has been decided based on the preliminary research results, that further measurements will be carried out on tablets prepared under fixed pressure (80 kN). High-

temperature measurements carried out on nontronite samples, showed that dehydration (deintercalation) occurs gradually, accompanied by a change in the number of water layers. It is directly related to the significant decrease in the measured electric permittivity as well as the extension of the relaxation time, which means that the decreasing interlayer distance slows down the reorientation of guest molecules. Therefore, the measurements were carried out in the temperature range for which the tested materials were stable, due to the amount of guest molecules bound in the interpackage spaces. The thermal stability of smectite modifications was obtained from thermogravimetric data.

Dielectric investigations were carried out in two scenarios. Firstly, dielectric measurements were performed at room temperature in the entire available frequency range of 25 Hz – 1 GHz. Then, tests were carried out as a function of temperature and in a narrower frequency range (25 Hz – 1 MHz). Dielectric dispersion and absorption were characterized by fitting the dielectric model, which allowed to obtain parameters describing these processes. The performed investigations allowed the analysis and description of the electrical properties of hydrated and modified smectites. All tested systems show a very strong increase in low-frequency permittivity, which was attributed to the surface and volume polarization resulting from free charge mobility (Maxwell – Wagner effect). The studied systems were characterized in terms of the occurrence of two relaxation processes: low-frequency (migration of ions on the surface of grains) and the process occurring in the radio frequency range, which was attributed to the movement of interpackage ions, as well as dipole relaxation. Processes in the kilo- and megahertz range were characterized by an average broadness of relaxation times ($\alpha \approx 0.35$) and were described using the Cole – Cole function. In the case of the tested intercalates, results of dielectric measurements indicated that the dielectric properties depend on the type of guest molecules. In most cases, at room temperature, the average relaxation time of the tested systems is approx. 1 μ s to approx. 10 μ s. The exceptions are nontronite and formamide-intercalated nontronite and montmorillonite, for which relaxation times are shorter, which means that they absorb electromagnetic radiation in the mega- and gigahertz range. It is assumed that the different hydration state of the examined smectites results in the extension of the relaxation time of montmorillonite in relation to nontronite. In smectites intercalated with formamide and its derivatives, an increase in the relaxation time with the increase in the size of the intercalant molecules was observed. This means that the presence of additional substituents delays the reorientation process of dipole guest molecules. The type of guest molecule also affects the dielectric increment value and the activation energy. The obtained activation energies vary

within fairly wide limits. For nontronite and montmorillonite intercalated with formamide, the activation energy was 80 kJ/mol and 65 kJ/mol, respectively. In comparison, 71 kJ/mol was obtained for hydrated nontronite, and 27 kJ/mol for its modification with *N*-ethylformamide. The observed differences in the activation energies may be caused by interactions of guest molecules with counterions in the ion solvation sphere, but also by hydrogen bonds with oxygen atoms of the mineral layers. No correlation was found between the $\Delta\varepsilon$ of the relaxation process in the radio frequency range and the dipole moment of the guest molecules. The Author of this dissertation does not consider the lack of correlation as evidence that dielectric relaxation is unrelated to the reorientation of guest molecules. Instead, the Author indicates the complex nature of relaxation, which consists of both guest reorientations and ion movements. The movements of dipoles are most likely correlated with the motions of counterions, which strongly influence the electrical polarization of the studied systems.

High-temperature studies of nontronite (25°C – 325°C) revealed changes in the dielectric curves of the system that were associated with the varying amounts of interlayer water present in the nontronite's interpackage spaces (two- and one-layer hydrates), which was a crucial observation. It has been noticed that the relaxation in the radio frequency range disappears with the complete removal of water molecules from the interpackage spaces. It indicates that the potential role of counterions as relaxants in the kilo-, megahertz range is dependent on the presence of guest molecules in the interpackage spaces of smectites. The absence of an intercalant (heated mineral) causes the limitation of ion mobility. Thus, the presence of guest molecules between mineral packages is necessary for the movement of counterions in the interpackage spaces.

The investigated montmorillonite and nontronite, as well as their intercalates with polar guest molecules, despite their low thermal stability, demonstrated interesting electric properties, indicating their potential applications.