

# Dielectric Response of Natural Clinoptilolite Type Zeolitic Material Containing Silver Iodide

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Natural zeolitic materials of the clinoptilolite type with regard to their dielectric properties were investigated. The coated samples of the clinoptilolite (CT) and its product containing silver iodide (CTAgI) in the form of the mixture of zeolitic powder and nonpolar paraffin oil were used. Clinoptilolite creates an inclusion compound with AgI where AgI can enter into the tunnels and can be deposited on the surface of clinoptilolite particles, too. Dielectric properties (complex permittivity  $\epsilon^*$  and loss factor  $\text{tg } \delta$ ) of the hydrated and dehydrated natural zeolite CT and its product CTAgI were investigated in the frequency range from  $10^1$  Hz to  $10^5$  Hz and at the temperatures from 20 °C to 70 °C. The conductivity of the CTAgI product was measured in the temperature range from 70 °C to 300 °C at the frequency 1 kHz, too.

Ionic conductivity and dielectric behaviour are among interesting features of various natural and synthetic zeolites [1–4]. Such knowledge about zeolites has become important because of their potential application in electrochemical devices. It has been shown that zeolites are ionic conductors and both ionic conductivity and dielectric relaxation at frequencies below 100 MHz are due to cation (proton) movement between preferred positions. Most of the zeolites, for which the ionic conductivity and dielectric behaviour have been reported, have been subject to ion exchange with varying amount of exchanged ions.

More than 30 natural zeolites have been characterized. The natural zeolitic material of the clinoptilolite (CT) type from Eastern Slovakia (Nižný Hrabovec) was the object of previous studies with respect to its ac and dc conductivity [5] and dielectric behaviour [6]. Being nontoxic materials, the natural zeolites are widely used in practice.

Zeolites are crystalline solids with molecular cavities joined into a three-dimensional network of silicon and aluminium interconnected by oxygen atoms. The internal surface of them is very high. For practical reason it is distinguished between large-pore zeolites (free diameter of about 0.8 nm) and small-pore zeolites with free diameter of about 0.4 nm. Because of three-dimensional system of the pores, zeolites are material-resistant to blockage of cation movement [7]. The cations placed in cages, which compensate the negative charges of the framework, are mobile and may move to new positions during dehydration and under the influence of an external electric field. They can be exchanged to varying degrees by the other cations or molecules without altering the structure of the zeo-

lite. Under the influence of the external electric field cations movement causes the electric charge transport and dielectric relaxation. Most zeolites, and exchanged too, contain more than one kind of ion in the internal free space.

In comparison to results of many authors [8–10], no relaxation process was visible on the plots of frequency dependences of imaginary part of complex permittivity  $\epsilon''$  and loss factor  $\text{tg } \delta$  measured in the frequency range from  $10^1$  Hz to  $10^5$  Hz and at the temperatures from 20 °C to 300 °C [6]. We supposed the absorption peak was covered by higher conductive losses. In the present work, in order to minimize the disturbing effect of the conductivity on dielectric relaxation, the coated samples (a mixture of zeolitic powder material and paraffin oil) were used.

Chemical, thermal, and structural analyses were done as well as ac and dc conductivity measurement results of iodine and silver forms of natural CT were studied in [5, 11–14].

It has been known for many years that AgI undergoes a phase transition at 146 °C which is connected with rapid increase of conductivity [15]. It was shown in [16] that in the case of composite material made up of AgI and the potassium form of the synthetic zeolite ZSM5, the phase transition of AgI influences even the properties of this synthetic zeolite. A sharp conductivity change occurred between 142 °C and 147 °C due to AgI undergoing the phase transition. In this material AgI forms thin conductive shell on the surface of the K-ZSM5 particles.

To spread the information about the natural CT behaviour and ion movement in it, this study of electrical and dielectric properties of natural clinoptilolite

type zeolitic material and that containing silver iodide was made.

## EXPERIMENTAL

### Material Preparation

For our study we used natural zeolite of the clinoptilolite type from East Slovakian deposit Nižný Hrabovec. According to analyses given in [17, 18] this natural zeolitic material contains 57.2 % of CT zeolite mineral on average. For the preparation of the natural zeolitic material of the clinoptilolite type containing AgI, the silver form of the natural zeolitic material AgCT described in [12] and potassium iodide solution were used. The obtained product was denoted as CTAgi. More detailed characterization of CTAgi (X-ray powder diffractometry, EDS analysis, scanning electron microscopy, IR spectroscopy, and thermal analysis) was given in [14]. Results of those analyses indicate that prepared CTAgi is an inclusion compound. Potassium iodide and other chemicals were all of anal. grade purity. AgI enters into tunnels and can be deposited on the surface of the particles, too. CTAgi contains on average 28.5 % AgI (13.1 % Ag and 15.4 % I).

### Sample Preparation

The zeolitic samples for electrical measurements were prepared in various forms:

Firstly – for better understanding of behaviour of CT zeolitic material containing AgI two pressed ( $\approx 250$  mg of powder zeolitic material pressed at 6.5 MPa) pellets, 12 mm in diameter, were prepared. One pellet was prepared from CTAgi and another was pressed from the physical mixture of pure CT and AgI with the same content of AgI (28.5 %), denoted as CT + AgI. The graphite emulsion was used as an electrode

material. Before measuring, the samples were held for 48 h at relative humidity 54 % obtained by using a saturated salt solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and at room temperature. The conductivity was measured at decreasing temperature and at the frequency  $f = 1$  kHz on the samples first heated to 300 °C. Measurements were performed in the air on the samples placed in a sample holder and put into a thermostat.

Secondly – approximately 250 mg of the CTAgi material was pressed at 6.5 MPa to form a pellet with diameter of 12 mm. The electrode material was Demetron silver paste E 4004 (Germany) heated for 10 min at  $\approx 250$  °C to make the electrodes conductive enough. Such samples were stored at room temperature and at RH about 54 %. Measurements were performed in the air.

Thirdly – powder zeolitic material was held for 24 h at  $\approx 54$  % RH. Experiments made in [4] showed that the water content in zeolitic sample would saturate after a few hundred min. After one day the nonpressed zeolitic powder was mixed with chemically inert non-polar paraffin oil with the volume ratio of the zeolitic powder to the oil equal to 3 : 7 to coat the sample. The mixture was filled into the measurement cell and put into a thermostat. Zeolitic material mixed with oil was not influenced by ambient humidity. The measurements were performed 24 h later in order the sedimentation might finish and the electrical parameters might stabilize.

Finally – powder zeolitic material was pretreated at 400 °C for 24 h in a flow of purified nitrogen. After the rapid cooling, the treatment followed as in the third case. Such zeolitic material was regarded to be dehydrated. The measurement cell was a home-made one. The description and parameters of the natural zeolitic samples used in this work for the study are given in Table 1.

Parallel capacitance  $C_p$  and conductance  $G_p$  were measured at temperatures as listed in Table 1 and at

Table 1. Characterization of Measured Samples

Sample	Water content	Electrodes	Temperature range	$\frac{E_A}{\text{eV}}$
1 pressed pellet CTAgI or CT + AgI	dehydrated at 300 °C	graphite emulsion	20–300 °C	
2 pressed pellet CTAgI	stored for 24 h at $\approx 54$ % RH	silver paste	25 °C	
3 CT powder + paraffin oil	stored for 24 h at $\approx 54$ % RH	measurement cell	20–70 °C	0.48
4 CT powder + paraffin oil	dehydrated at 400 °C	measurement cell	20–70 °C	
4 CTAgi powder + paraffin oil	dehydrated at 400 °C	measurement cell	20–70 °C	0.66

frequencies ranged from  $10^1$  Hz to  $10^5$  Hz using General Radio Precision Capacitance Bridge Model 1616. The temperature was kept constant with an accuracy of  $1^\circ\text{C}$  and measured using Cu—CuNi thermocouple. The end of the thermocouple was placed as near as possible to the sample. Measurements were performed at an applied ac voltage 1 V (pressed pellet) and 2 V (measurement cell).

The complex permittivity  $\varepsilon^* = \varepsilon' - i\varepsilon''$  and loss factor  $\text{tg } \delta$  were calculated from measured values of  $C_p$ ,  $G_p$  and the sample geometry.

## RESULTS AND DISCUSSION

The dielectric relaxation in zeolites is provoked by a change of dipole moment vector, formed between the cations in cavities and lattice (framework) anion when the cations migrate. Absorbed polar water affects the relaxation, too. Natural zeolites exhibit complex cation distribution in comparison with most of synthetic zeolites which are monocationic or dicationic.

The temperature dependences of conductivity measured at the frequency 1 kHz of both CTAgl and CT + AgI samples are in Fig. 1. The samples in the form of pressed pellets were heated to  $300^\circ\text{C}$  and then measured at temperatures decreasing to  $70^\circ\text{C}$  in order to avoid the changes connected with water content in zeolitic material. The conductivity of CTAgl is about one order higher than the conductivity of CT + AgI when the content of AgI was the same (28.5 %). No expected drop of conductivity at about  $146^\circ\text{C}$  appeared. It is possible that the CT + AgI mixture can be partially changed when heated to  $300^\circ\text{C}$ . Such effect in the case of hydrated mordenite—AgI inclusion compound is mentioned in [19]. More detailed study of the physical mixture CT + AgI should be done in the following paper.

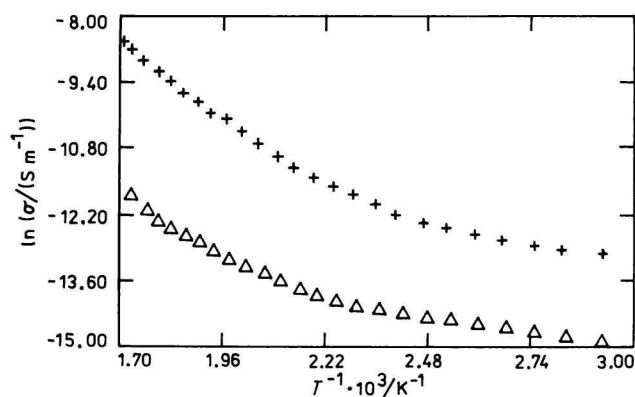


Fig. 1. Temperature dependences of the conductivity of CT + AgI ( $\Delta$ ) and CTAgl (+) measured on the pressed samples at the frequency  $f = 1$  kHz.

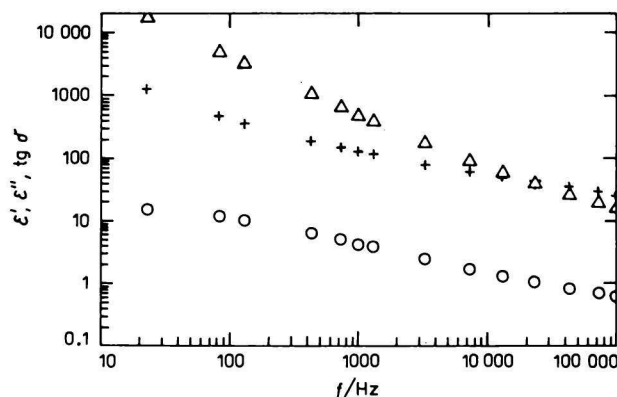


Fig. 2. Dielectric behaviour,  $\varepsilon'$  (+),  $\varepsilon''$  ( $\Delta$ ), and  $\text{tg } \delta$  (O) of the pressed nonexchanged CT sample at the temperature  $\theta = 25^\circ\text{C}$  and at frequencies from  $10^1$  Hz to  $10^5$  Hz.

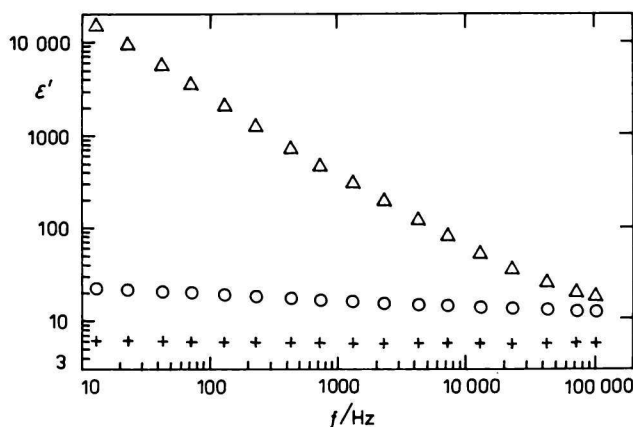


Fig. 3. Frequency dependences of relative permittivity  $\varepsilon'$  at the temperature  $\theta = 23^\circ\text{C}$ . + dehydrated CT,  $\Delta$  hydrated CT, and O dehydrated CTAgl.

Dielectric behaviour of the pressed CTAgl sample at  $25^\circ\text{C}$  is shown in Fig. 2. Dielectric parameters – real and imaginary parts of complex permittivity  $\varepsilon'$  and  $\varepsilon''$  and loss factor  $\text{tg } \delta$  were calculated from the measured values  $C_p$  and  $G_p$  and the sample geometry. Both parameters  $C_p$  and  $G_p$  are strongly frequency-dependent at all measured samples. The  $\varepsilon'' = f(f)$  and  $\text{tg } \delta = f(f)$  are those as typical for dielectric material with hopping carriers or the loss peak is covered with prevailing conductive losses. No polarization peak, usually observable on zeolitic material under similar circumstances, was found on  $\varepsilon'' = f(f)$  and  $\text{tg } \delta = f(f)$  curves in Fig. 2. We have to remark that the polarization peak could appear at higher frequencies than  $10^5$  Hz or at lower frequencies than 10 Hz. The same behaviour was observed at copper-exchanged CT at broad interval of the temperatures [6].

Fig. 3 shows the frequency dependences of the real part of the complex permittivity  $\varepsilon' = f(f)$  of the mea-

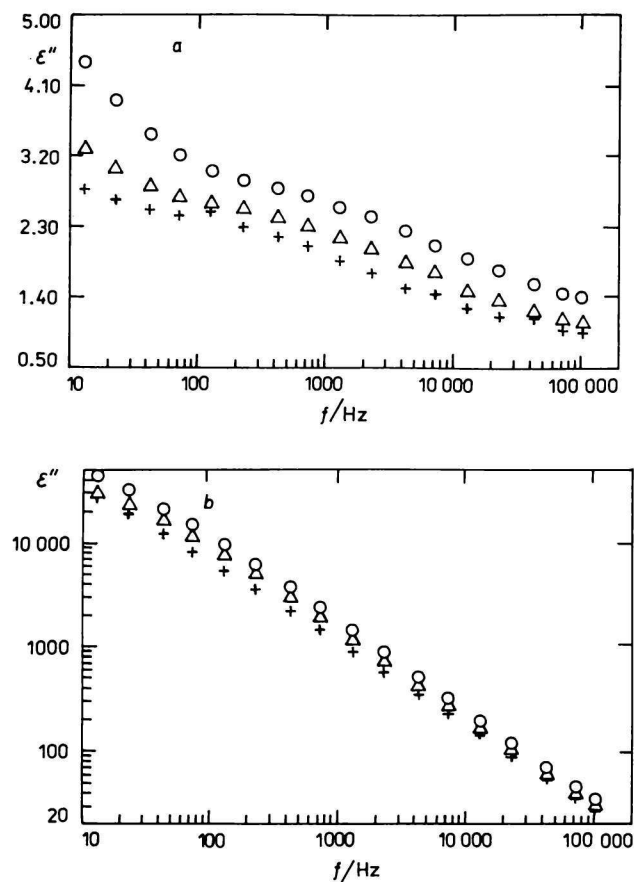


Fig. 4. Frequency dependences of the imaginary part  $\varepsilon''$  of the complex permittivity. a) Measured on the dehydrated CTAgl powder sample at the temperatures 23°C (+), 36°C ( $\Delta$ ), 49°C ( $\circ$ ); b) measured on the hydrated nonexchanged powder CT sample at the temperatures 23°C (+), 39°C ( $\Delta$ ), 45°C ( $\circ$ ).

sured samples at the temperature 23°C. At the high frequency end the relative permittivity  $\varepsilon'$  tends towards its optical limit which is more evident at hydrated CT and dehydrated CTAgl sample than at dehydrated CT sample.

Very broad loss peak with low intensity appears at the dependences of the imaginary part  $\varepsilon''$  of the complex permittivity *vs.* frequency obtained on the dehydrated CTAgl coated powder sample as one can see in Fig. 4a. The same dependences obtained on the hydrated (Fig. 4b) and dehydrated (not shown) CT coated powder sample do not show any peak in the interval of frequencies from  $10^1$  Hz to  $10^5$  Hz.

In order to find any possibility to characterize the dielectric behaviour of measured samples, the  $\text{tg } \delta$  values were calculated at the frequencies ranged from  $10^1$  Hz to  $10^5$  Hz at measured temperatures in the interval from 23°C to 70°C, too. Such curves are shown in Fig. 5a (dehydrated coated powder CT), Fig. 5b (hydrated coated powder CT), and Fig. 5c (dehydrated CTAgl coated powder). The dielectric behaviour shown in Figs. 5b and 5c exhibits one dielectric relaxation (one

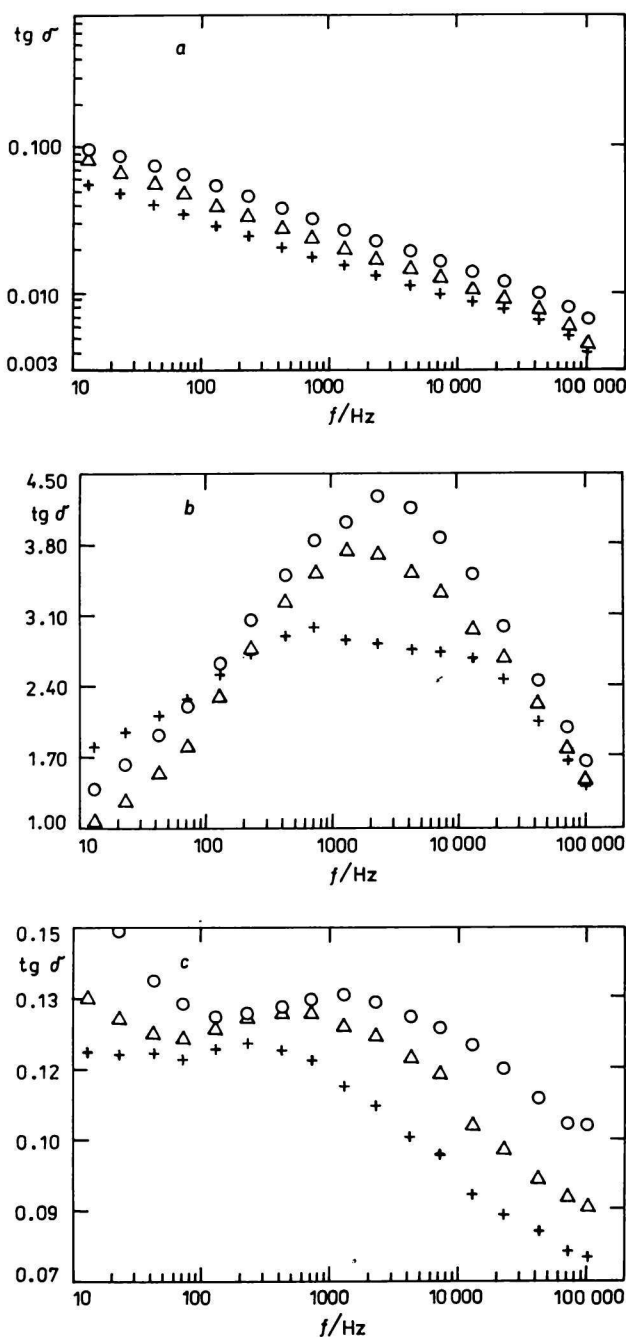


Fig. 5. Calculated values of the loss factor  $\text{tg } \delta$  in the frequency range  $10^1$  Hz to  $10^5$  Hz, a) of the dehydrated nonexchanged CT powder sample at the temperatures 23°C (+), 35°C ( $\Delta$ ), 45°C ( $\circ$ ), b) of the hydrated CT powder sample at the temperatures 23°C (+), 35°C ( $\Delta$ ), 45°C ( $\circ$ ), c) of the dehydrated CTAgl powder sample at the temperatures 23°C (+), 36°C ( $\Delta$ ), 49°C ( $\circ$ ).

absorption peak) on the frequency dependence of the loss factor  $\text{tg } \delta$ . The plots are shifted to the higher frequency with the rising temperature. The intensity of the relaxation depends on the temperature, too.

Following the equation

$$f_m = f_0 \varepsilon_s / \varepsilon_\infty \exp(-E_A/kT),$$

where  $f_m$  is the frequency in the maximum of the

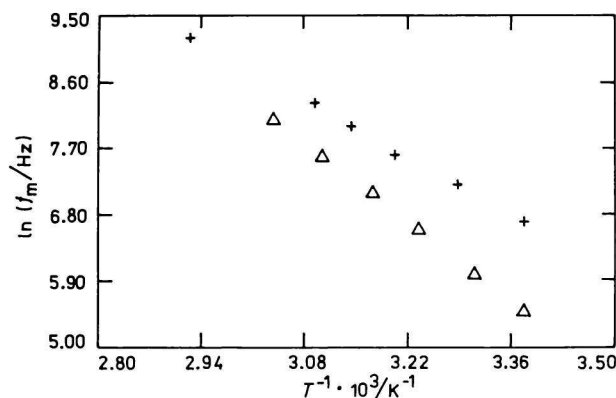


Fig. 6. Temperature dependences of  $f_m$  of the hydrated CT (+) powder sample and dehydrated CTAgl ( $\Delta$ ) powder sample.

curve  $\text{tg } \delta = f(f)$ ,  $f_0$  is a constant,  $\epsilon_s$  and  $\epsilon_\infty$  are the static and optical value of the relative permittivity, respectively,  $k$  is the Boltzmann constant, and  $T$  is the measurement temperature ( $T/K$ ), the activation energy  $E_A$  of the relaxation was determined from the slope of the Arrhenius plot. Preexponential factor was not calculated. The dielectric relaxation can be partly characterized with the experimental parameters  $f_m$  and activation energy  $E_A$ . These parameters characterize the mean reorientation velocity for the dipoles and the mean mobility for the cations in the cavities.

The critical frequencies  $f_m$  of the  $\text{tg } \delta = f(f)$  curves obtained at CTAgl (Fig. 5c) in comparison to those obtained at hydrated CT (Fig. 5b) are shifted to the lower values when the temperature is a parameter. The dielectric loss of hydrated CT is higher (one order) than those found at dehydrated CT and dehydrated CTAgl samples. Such a rise of dielectric loss is due to higher electric conduction of the hydrated CT sample. The Arrhenius plots (Fig. 6) were constructed using the  $f_m$  values in Figs. 5b and 5c. Arrhenius plot can be well linearly approximated. Correlation coefficients of the Arrhenius plot  $r = 0.998$  and  $r = 0.995$  and activation energy  $E_A = 0.48$  eV and  $E_A = 0.66$  eV were calculated for the hydrated coated powder CT sample and dehydrated CTAgl coated powder sample, respectively.

Dielectric absorption at frequencies lower than 100 MHz (intermediate frequencies) is referred as absorption (domain) II [10, 20]. The rise of dielectric loss and  $\epsilon''$  at the low-frequency end of their frequency dependence is often regarded to be the result of an electrode polarization or the Maxwell—Wagner effect [9, 21]. On the other hand, the concept of low-frequency dispersion was brought in [4, 22] to describe the processes at the low-frequency end of  $\epsilon'' = f(f)$  dependence. An important conclusion was drawn that the low-frequency phenomena in zeolites are genuinely volume processes and are not confined to the electrodes. Such

behaviour was found in systems in which slowly mobile charge carriers dominate the dielectric behaviour. The components of  $\epsilon^*$  increase towards low frequencies with no sign of saturation. Such behaviour is seen e.g. in Fig. 4a. Low-frequency dispersion was regarded to be dominated by large displacement of charges between cavities.

One of the aspects which have to be taken into account to evaluate the dielectric behaviour of the zeolites is their chemical composition [23]. The framework composition of the natural CT is more complicated than in the case of the synthetic zeolites. More oxides than only those of Al and Si enter the natural CT framework structure. On the other hand, the cationic composition in intrazeolitic space plays an important role, too. The existence of correlated movement of the intrazeolitic cations was stressed in [10]. Cations create “small” microscopic objects called clusters which are considered as units of relaxation. Under the effect of fluctuation and varying surrounding the dipole moments of various clusters vary, too. Thermal movement can redistribute the cations inside a cluster. So, different sets of clusters will have different mean frequency of relaxation.

Comparing Figs. 5a, 5b, and 5c one can see that the presence of AgI and/or absorbed water molecules in the cavities of the zeolite gives rise to the polarization on the  $\text{tg } \delta$  plots in the frequency range between  $10^1$  Hz to  $10^5$  Hz. The polarization peak of CTAgl visible on the frequency dependence of  $\epsilon''$  is a broad one. It can be the result of either the broad distribution of relaxation times influenced by above-mentioned circumstances or the superposition of more relaxations with relaxation times close to each other.

Local jumps of the cations over two neighbouring sites in the cages are considered to be responsible for the polarization process. Rising temperature facilitates the cation movement and the polarization peak appears at higher frequency. Also the water present in the cavities of zeolites is very effective to change the mobility of positive ions and thus to influence the conductivity and dielectric behaviour of them.

The water present in hydrated CT can facilitate the movement of some metallic ions which natural CT contains in its cavities and the polarization peak appears. Another possibility giving rise to the polarization are water molecules themselves. Krogh Andersen *et al.* [1] concluded that protons and/or hydroxyl ions contribute to the conductivity in hydrated zeolites. Evidence for the polarization due to the reorientation of water molecules is given in [10, 24] but the polarization peak is always situated at high frequencies (about  $10^9$  Hz). As it is pointed out in [7], zeolites can contain different types of water. Some of the water molecules are not linked to the framework and other can be hydrogen-bonded to oxygens of the framework. To evaluate this one needs to make more detailed spectroscopic studies.



## CONCLUSION

Results of our measurements indicate that the AgI form of natural clinoptilolite should be a new inclusion compound. No conductivity drop characteristic of AgI at about 146°C appeared at our samples of CTAgl and CT + AgI. The aim of this study was to characterize electrical and dielectric properties of these compounds.

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