

# Dielectrical Behaviour and Conductivity of Natural Copper Exchanged Clinoptilolite

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The aim of this study was to characterize electrical conductivity and dielectrical properties of the Cu(II) exchanged zeolite — natural clinoptilolite from Eastern Slovakia in the range of frequencies from  $10^1$  to  $10^5$  Hz and at temperatures from 218 to 603 K. The measured values of the conductivity  $\sigma$  ranged from  $10^{-10}$  to  $10^{-5}$  S  $m^{-1}$  at these frequencies and those temperatures. Dielectrical loss peak was found only at temperatures lower than 273 K. Activation energy calculated using static values  $\sigma_s$  extrapolated from Cole—Cole impedance diagrams was found to be  $E_a = 0.78$  eV. The results of Electron Microsonda measurements, CHN analyses, and thermal analyses are given, too.

Zeolites are crystalline aluminosilicates composed of cations (metal ions, ammonium ions or hydrogen ions) and an aluminosilicate anion framework. The formula for zeolites is  $M_x/m[(AlO_2)_x(SiO_2)_y] \cdot nH_2O$ , where M is a cation with valence  $m$ . In square parenthesis the anion framework forms channels and cages in which M ions and absorbed molecules are located. The natural zeolites usually contain more metal ions.

By the sorption of different molecules or ions in the natural clinoptilolite (CT) a number of new products (new inclusion compounds) were prepared [1]. We enclosed e.g. the nutritive ions or all their molecules (KCl), different agrochemicals, iodine and its ions, tetracyano complexes, cyclodextrins, etc. Some of them were prepared in analogous way also from the synthetic zeolites. In some cases the sorption of Cu(II) or Ca(II) ions affected positively the amount of the new sorbate. This effect was observed mainly in the case of cyclodextrins [2]. According to the literature [3] some intrazeolitic sorption of metallic ions (copper ions inclusive) into the zeolitic host is known. This occurs besides the substitution in the cationic part of the zeolitic host.

Conductivity and relaxation properties of various types of zeolites exchanged with monovalent or divalent cations have been extensively studied and results published in the literature [4—8]. In particular, it has been shown that both ionic conductivity and dielectric relaxation are due to cation jumps. The analysis of these studies shows that they are often carried out in different experimental conditions, so the obtained results are difficult to compare. It is generally admitted that the dielectric relaxation and conduction phenomena observed at frequencies below

100 MHz (the so-called intermediate frequencies) are related to the movements of cations in the large cavities and channels in which the mentioned cations can be introduced and where they can move between preferred positions. The polarization effects are visible in the frequency dependence of imaginary part of complex permittivity  $\epsilon'' = f(f)$  or in frequency dependence of loss tangent  $\tan \delta = f(f)$  creating one or more peaks. These peaks can be characterized by critical frequency and the intensity (maximum). It is well known that the absorbed molecules or exchanged cations influence the conductivity and the relaxation properties of zeolites [4—7]. In general, there are following aspects which must be taken into account:

- chemical composition of the zeolite with respect to the relation  $n(Si)/n(Al)$ ,
- properties and influence of the exchanged cations,
- the contents of the humidity,
- the temperature of the sample [8].

Investigation of the dielectrical and electrical properties of the natural zeolitic material containing Cu(II) ions is a continuation of the study of the natural clinoptilolite type zeolite from Nižný Hrabovec (Eastern Slovakia). Its practical use and possibility of the exploitation were studied in [9, 10]. The conductivity of this natural zeolitic material of the clinoptilolite type ranged from  $10^{-8}$  to  $8 \times 10^{-6}$  S  $cm^{-1}$  at the temperature 293 K and different relative humidities (75 to 11 %) [11].

In this paper dielectrical properties and conductivity of the copper form of the natural CT-type zeolite in the temperature interval from 218 to 603 K were studied.

## EXPERIMENTAL

For our study we used natural zeolite of the clinoptilolite type (CT) from East Slovakian deposit in Nižný Hrabovec. This natural zeolitic material contains on average 57.2 % of the CT zeolitic mineral [12].

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and other chemicals were all of anal. grade purity (Lachema, Brno).

The natural zeolite was dried at 100–110 °C for 1 h. 5 g of this partially thermal activated zeolite was mixed with 20 cm<sup>3</sup> of 1 M- $\text{CuSO}_4$  solution. The heterogeneous mixture of the zeolite and  $\text{CuSO}_4$  solution was left to stand for ten days (with occasional mixing). After ten days the heterogeneous mixture was decanted three times with distilled water and centrifuged (the content of copper ions in water after decantation was checked by analytical method). The zeolitic product was dried at 70 °C. This product will be indicated as CTCu.

The copper content and other elements were determined by Electron Microsonda measurements (JXA-5A) applying KeveX. Parameters used: accelerating voltage 25 kV, sample current  $1.5 \times 10^{-7}$  A, analyzing crystal LiF-PED. CHN analyses were performed by Perkin—Elmer 2400 elemental analyzer.

The thermal analyses (TG, DTA, and DTG) were measured up to 900 °C in air on a derivatograph MOM OD 102 (Paulik—Paulik—Erdey, Budapest), weight of the sample 100 mg, sensitivities: TG 100 mg, DTA 1/5, DTG 1/5, heating rate 9 °C min<sup>-1</sup>, reference material  $\text{Al}_2\text{O}_3$ .

IR spectra were obtained by KBr disc technique using a Specord M 80 IR spectrometer (Zeiss, Jena).

The samples used for the electrical measurements were in the form of a pellet with diameter of 12 mm and  $\approx 1.5$  mm thick pressed at 6.5 MPa ( $\approx 300$  mg of the material) by a Zeiss (Jena) press.

Both the sides of the prepared pellet were coated with Demetron silver paste E 4004 (Germany) and heated for 10 min at 250 °C to make the electrode conductive enough. The whole back side of the pellets was coated. The diameter of upper electrode was about 7.2 mm. To have a good electrical contact the measured sample was placed into sample holder with two opposite stainless steel electrodes pressed against the sample.

Parallel capacitance  $C_p$  and conductance  $G_p$  were measured at temperatures between 218 and 603 K and frequencies ranged from 10 to 10<sup>5</sup> Hz in air using General Radio Capacitance Bridge 1616 and Tesla BM 595 RLC meter. The temperature was kept constant with an accuracy of 1 K 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. The ac applied voltage had to be higher

at lower temperatures (up to 5 V) to ensure better sensitivity of the apparatus. The complex impedance and complex permittivity were calculated from measured values of  $C_p$  and  $G_p$  at temperatures between 218 K and 603 K and frequencies between 10 Hz and 10<sup>5</sup> Hz.

In the samples the content of the humidity decreases with increasing temperature. In order to exclude this effect, during each measurement the sample was heated to the highest temperature 603 K and stabilized for 2 h. After this time measured parameters were constant at constant temperature.

## RESULTS

The contents in mass % of copper and other elements in prepared copper exchanged CT zeolitic (CTCu) product were determined by Electron Microsonda measurements ( $\text{SiO}_2$ : 41.58 %,  $\text{Al}_2\text{O}_3$ : 6.87 %,  $\text{K}_2\text{O}$ : 4.37 %,  $\text{CaO}$ : 4.03 %,  $\text{FeO} + \text{Fe}_2\text{O}_3$ : 8.33 %,  $\text{Cu}$ : 34.82 %). Results obtained by CHN analysis (hydrogen: 1.1 %) showed that the CTCu product contains 9.9 % of water.

Only some less significant changes were observed by examining the IR spectra of the original zeolite and its CTCu product (Fig. 1). The changes appeared in the bands in the  $\tilde{\nu}$  region at 900–1200 cm<sup>-1</sup>, which corresponds to the asymmetric stretching vibration of the (Al, Si)O group.

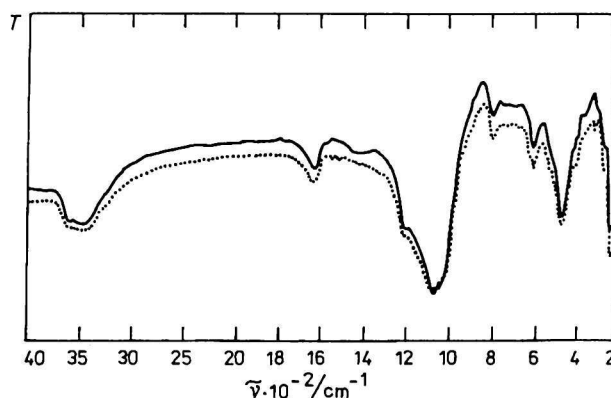


Fig. 1. IR spectra of the original natural CT zeolitic material (—) and CTCu product (.....).

According to the results of the thermal analysis (Fig. 2) the mass loss due to the guest water in the zeolitic material is 9.4 % up to 603 K.

The ac conductivity was measured separately at 1 kHz at temperatures increasing up to 603 K and against at decreasing temperatures. In order to find out the dc conductivity, the frequency dependences of equivalent parallel capacitance  $C_p$  and equivalent parallel conductance  $G_p$  were measured in the range of frequencies from 10<sup>1</sup> to 10<sup>5</sup> Hz at constant tem-

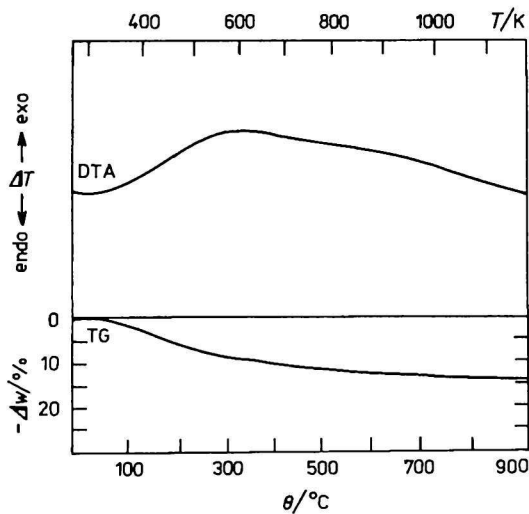


Fig. 2. TG and DTA curves of CTCu product.

quency-dependent as well (Fig. 3). Real and imaginary parts of complex impedance  $Z'$  and  $Z''$  were calculated. It is possible to obtain the static value of conductivity  $\sigma_s$  from the  $Z'' = f(Z')$  plot when the frequency rises from lower to upper limit at constant temperature.  $\sigma_s$  value is found using extrapolated value  $Z_s$  when the dependence  $Z'' = f(Z')$  has semi-circular shape [13]. Complex impedance plot at temperatures higher than 473 K creates very good expressed semicircle with the centre shifted below the real axis (Fig. 4a). The static value  $Z_s$  can be found by the extrapolation on low frequency side of the plot. It was not possible to find  $Z_s$  at temperatures below the temperature 473 K or it could be found with very low precision only as it is seen in Fig. 4b.

The Arrhenius plots were constructed for the measured values of conductivity (frequency  $f = 1$  kHz)

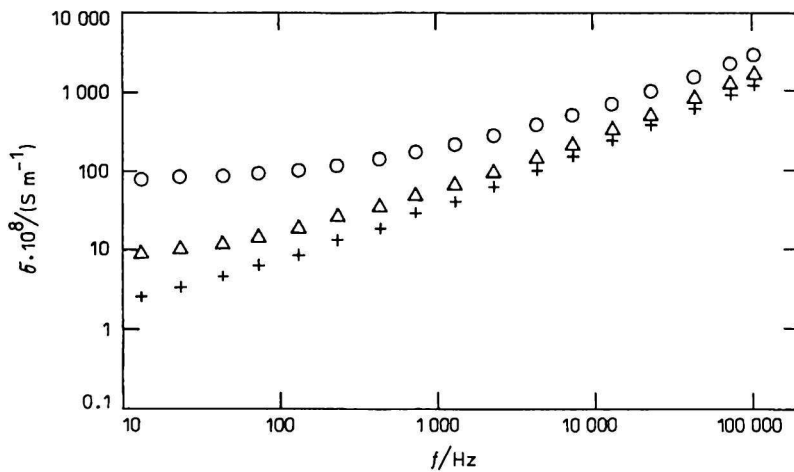


Fig. 3. Frequency dependences of the conductivity of CTCu-type zeolite at various temperatures. + 437.5 K, n 482 K, s 555 K.

peratures up to 555 K. Both parameters  $C_p$  and  $G_p$  of natural clinoptilolite are strongly frequency-dependent at all temperatures. Following this, the calculated values of conductivity  $\sigma$  are strongly fre-

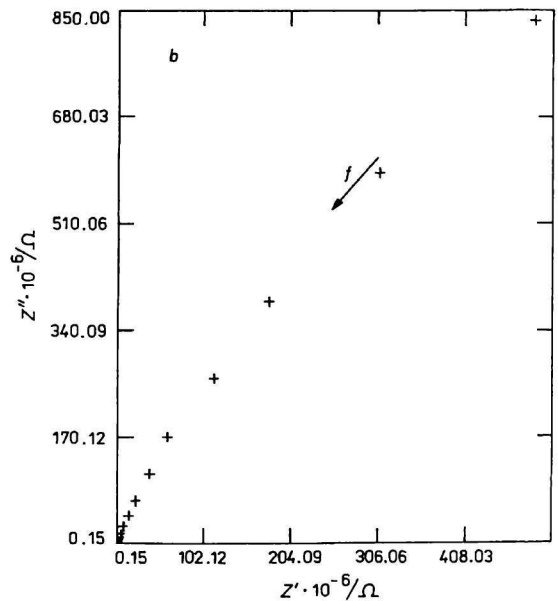
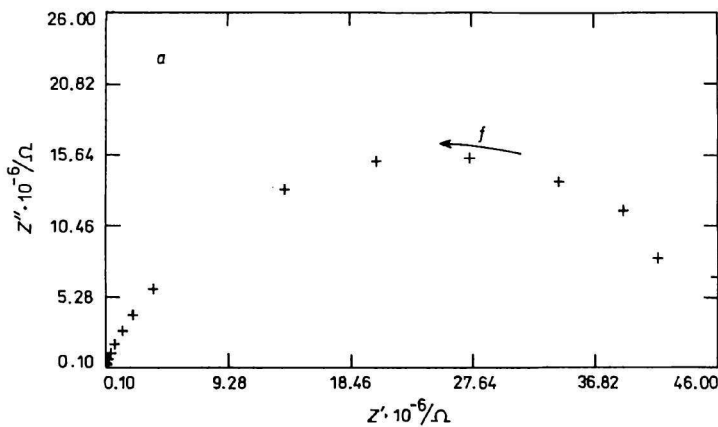


Fig. 4. Complex impedance diagrams of CTCu-type zeolite at a) + 555 K and b) + 418.5 K.

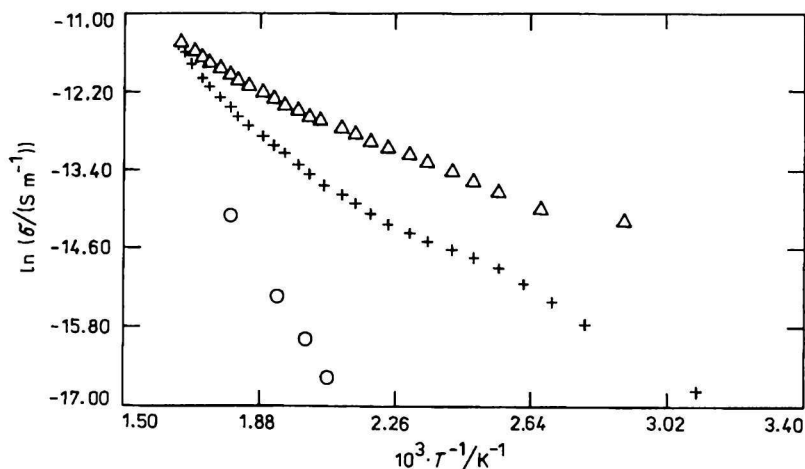


Fig. 5. Arrhenius plots of CTCu-type zeolite at 1 kHz ( $\Delta$  rising temperature, + decreasing temperature) and the calculated one using  $Z_s$  values from the Cole—Cole plots ( $\circ$ ).

at increasing and decreasing temperature. The results are shown in Fig. 5. The Arrhenius plot of static values  $\sigma_s$  extrapolated from Cole—Cole impedance diagrams at temperatures higher than 473 K is in Fig. 5 as well. Three parts with various activation energies  $E_a = 0.19$  eV, 0.27 eV, and 0.44 eV are visible at the conductivity plot measured at the frequency 1 kHz when the temperature is decreasing from the highest value. The activation energy of  $\sigma_s$   $E_a = 0.78$  eV was found using values  $Z_s$  found at complex impedance Cole—Cole plots of Cu(II) exchanged CT at temperatures from 473 to 555 K when Cole—Cole plots were constructed.

Dielectric parameters — real and imaginary parts of complex permittivity  $\epsilon'$  and  $\epsilon''$  ( $\epsilon' \equiv \epsilon_r$ ) and loss tangent  $\text{tg } \delta$  were calculated from the measured values of  $C_p$  and  $G_p$  and the sample geometry. The frequency dependences of  $\epsilon'$  are shown in Fig. 6. The real part of complex permittivity  $\epsilon'$  found at the high frequency end of the used frequency range limits to

the values from 8 to 16 at measured temperature range from 218 to 603 K. The  $\epsilon'' = f(f)$  dependences (Fig. 7) show typical behaviour of dielectric material with hopping carriers with prevailing conductivity mechanism [14]. No influence of the polarization is visible at these curves. The frequency dependences of the loss tangent  $\text{tg } \delta = f(f)$  (not represented) show the same behaviour without a loss peak as  $\epsilon'' = f(f)$ . Another  $\epsilon''$  behaviour was found at temperatures below 273 K and frequencies ranged from 10 to  $10^5$  Hz as it can be seen in Fig. 8. The polarization peak appeared at these temperatures. With increasing temperature the maximum is shifted to the higher frequencies. The height of the polarization peak is changed as the temperature is changed, too.

In order to ensure the time stability, the dielectric parameters were measured in the same way as the conduction starting from the highest value of temperature.

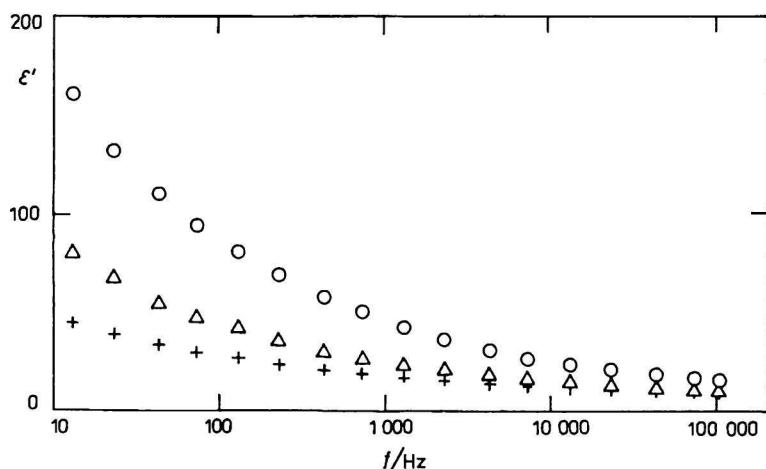


Fig. 6. Frequency dependences of the real part of permittivity of CTCu-type zeolite at various temperatures. + 418.5 K,  $\Delta$  482 K,  $\circ$  555 K.

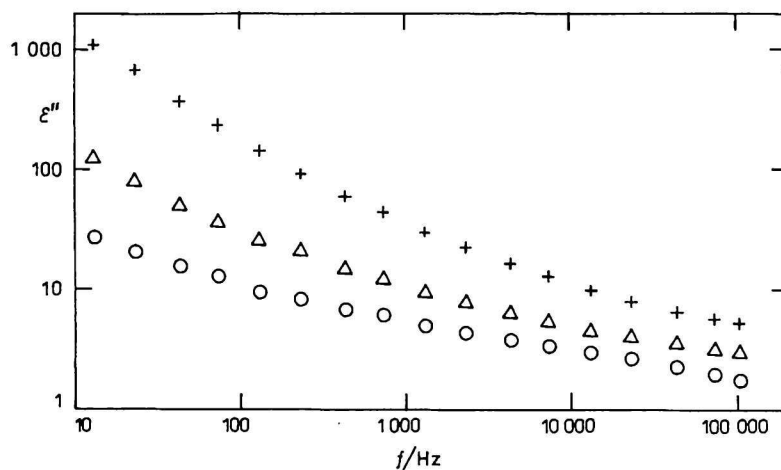


Fig. 7. Frequency dependences of the imaginary part of permittivity of CTCu-type zeolite at various temperatures. + 418.5 K,  $\Delta$  482 K,  $\circ$  555 K.

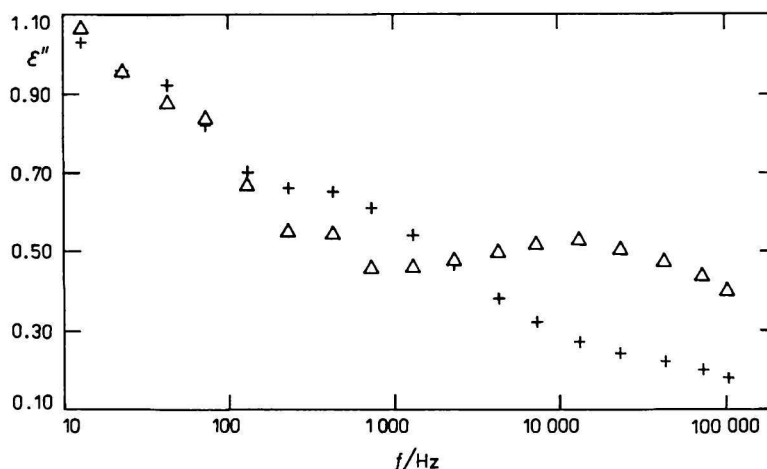


Fig. 8. Frequency dependence of the imaginary part of permittivity of CTCu-type zeolite at 218 K (+) and 253 K ( $\Delta$ ).

## DISCUSSION

By putting the zeolitic material into contact with the solution of  $\text{CuSO}_4$  we obtained CTCu zeolitic product.  $\text{Cu(II)}$  ions were sorbed into the zeolitic material.

The chemical composition [12, 15] of the starting zeolitic CT material agreed with the results obtained from the Electron Microsonda measurements and CHN analysis [11]. The results of CHN analysis confirmed that the content of water in the original zeolite amounted to 10.5 % (the value mentioned in [12, 15] is 8.97–10.9 %). The CTCu zeolitic product contains also the water but in a lower amount (9.9 %). One part of water was substituted by intrazeolitic copper cations.

According to the results of the Electron Microsonda measurements and CHN analysis an average copper content of CTCu product was 31.7 % (at 293 K). The content of the  $\text{Cu(II)}$  ions depends on the mode of the preparation. The presence of  $\text{Cu(II)}$  ions in the CTCu zeolitic product was also observed ac-

ording to the colour. After the sorption of  $\text{Cu(II)}$  ions into the zeolite, the colour of this product was slightly blue.

Diffraction measurements of CT zeolitic material and its CTCu product as well as those of the CTCu zeolite with other organic molecules were described in the literature [2].

No significant changes were observed by examining the infrared spectra of the original zeolite and its CTCu product. A certain change (Fig. 1) appeared in the  $\tilde{\nu}$  band at 900–1200  $\text{cm}^{-1}$  vibration of the (Al, Si)O group (this band changes from a sharp to a broader one). Such changes of this band were found also in other zeolitic product prepared as a consequence of the sorption of different organic and inorganic compounds in the microcrystalline zeolitic material [1, 2].

It is known from the literature [16] that during the heating of the natural zeolite up to 1173 K 9.4 % of the total water was released. The original water content was 10.9 %. The zeolite contained 1.5 % of its original water content after heating to 1173 K. The

partial mass loss up to 608 K was 9.2 %. Similarly the zeolitic product containing iodine and its ions [11, 17] partially released iodine during the thermal analysis. In our case after the heating of the CTCu product up to 603 K the mass loss was 9.3 % (the total content of water was 9.9 %). A small amount of water was still included in the zeolite.

As mentioned before, the conductivity measured in natural clinoptilolite pellets is superposed of an ac and dc conductivity. That means that they are both active. The measured value tends towards its static limit at a low frequency. Because of electrode—dielectric interface effects, it can be difficult to measure the dc conductivity directly. There is a simple method to find the static value of the conductivity  $\sigma_s$  using a complex impedance plot but the electrode material plays a significant role [13].

Conductivity of the zeolites is ionic. Regarding Fig. 5 we suppose that more types of conduction mechanisms could be present at various temperatures. There are three areas with various activation energy found in Fig. 5. The activation energy calculated from  $\sigma_s$  values found at the Cole—Cole impedance plot as regards the geometry of the pellets is higher than those calculated at 1 kHz when ac conductivity is present, too. The ions responsible for the conductivity are strongly influenced by their surroundings. Their motion is highly correlated with other ions present in the cavities [8, 18].

The  $\sigma_s$  values used to calculate the dc conductivity activation energy were extrapolated for the temperatures higher than 473 K only. The shape of the Cole—Cole impedance plot is influenced by dielectric—electrode interface on its low frequency side. The dielectric—electrode interface effects deteriorate the possibility to evaluate dc conductivity. We suppose that this is the case at the lower temperatures and such a behaviour is seen in Fig. 4b. The influence of zeolite—electrode interface is lower at higher temperatures so the impedance approaches its  $Z_s$  value as it is seen in Fig. 4a. Then the  $Z_s$  value can be extrapolated and  $\sigma_s$  calculated with higher accuracy.

The frequency dependences of the imaginary part of permittivity in Fig. 7 show the behaviour typical for hopping conductivity mechanism of ionic conductor. No polarization characteristic of zeolitic material at used intermediate frequencies of the measuring ac signal ( $10^1$ — $10^5$  Hz) was observed. It was pointed

out in [5] that the samples prepared in the form of pressed pellets are often not convenient for dielectric absorption measurement because the loss peak can be covered with high conduction losses. This assumption was fulfilled in our case when no peak appeared at  $\epsilon'' = f(f)$  plots (Fig. 7). The relaxation process caused by the migration of the ions appeared at very low temperatures (lower than 273 K). This is shown in Fig. 8. When the temperature decreased, the conductivity dropped as well and the relaxation peak would appear at the  $\epsilon'' = f(f)$  plot. This relaxation is characterized by an absorption peak (temperature-dependent intensity and distribution of the relaxation times). No polarization peak was found at the room temperature, either.

## REFERENCES

1. Sopková, A., *J. Incl. Phenom.* 14, 5 (1992).
2. Mondík, P., Sopková, A., Suchár, G., and Wadsten, T., *J. Incl. Phenom.* 13, 109 (1992).
3. Scholhorn, R., in *Inclusion Compounds*, Vol. 1. (Atwood, J. L., Davies, J. E. D., and MacNicol, D. D., Editors.) P. 260. Academic Press, London, 1984.
4. Schoonheydt, R. A. and de Wilde, W., *J. Chem. Soc., Faraday Trans. 1* 70, 2132 (1974).
5. Tabourier, P., Carru, J. C., and Wacrenier, J. M., *Zeolites* 3, 50 (1983).
6. Tabourier, P., Carru, J. C., and Wacrenier, J. M., *J. Chim. Phys.* 87, 43 (1990).
7. Krogh Andersen, E., Krogh Andersen, I. G., and Skou, E., in *Proton Conductors*. (Colomban, Ph., Editor.) P. 210. Cambridge University Press, Cambridge, 1992.
8. Carru, J. C., Tabourier, P., and Wacrenier, J. M., *J. Chim. Phys.* 88, 307 (1991).
9. Bubanec, J. and Sopková, A., *Chem. Prům.* 38, 11 (1988).
10. Šingliar, M., Sopková, A., Bubanec, J., and Fabián, P., *Agrochemia* (Bratislava) 32, 91 (1992).
11. Reháková, M., Sopková, A., Casciola, M., and Bastl, Z., *Solid State Ionics* 66, 189 (1993).
12. Sopková, A., Bubanec, J., and Mihalič, A., *Rudy* 10, 298 (1988).
13. Bauerle, J. E., *J. Phys. Chem. Solids* 30, 2657 (1969).
14. Jonscher, A. K., *The Universal Dielectric Response — a Review of Data and Their New Interpretation*. Academic Press, London, 1980.
15. Horvathová, E., *Chem. Prům.* 38, 351 (1988).
16. Pechar, F. and Rykl, D., *Geologica Carpathica* 32, 211 (1982).
17. Reháková, M., Sopková, A., and Lokaj, J., *J. Incl. Phenom.* 14, 47 (1992).
18. Schoonheydt, R. A. and Velghe, F., *J. Chem. Soc., Faraday Trans. 1* 72, 172 (1975).

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