

# Influence of density and water vapor content on the dielectric response of natural zeolites

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Dielectric spectra of natural zeolite (clinoptilolite) are studied in a wide range of pressures from  $10^{-2}$  Torr up to atmospheric pressure and the absorption IR spectra of clinoptilolite (Cl) have been investigated from 4000 to  $400\text{ cm}^{-1}$ . The measurements were carried out on samples of high density (natural plate) and low density (unpressed powder). It is established that the frequency dependence of both real and imaginary parts of the dielectric permittivity is characterized by approximately the same relaxation time of about  $10^{-5}$  s. It is concluded that in all these cases, the dielectric spectra are determined by fluctuations of alkali-metal ions associated with the water molecules inside the zeolite pores. A difference in the corresponding dielectric spectra is related to the concentration of these complexes. In the IR spectra, it is established that the presence of coordinating water and its large width evidences on localization of (OH) groups in the channels.

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## 1. Introduction

Zeolites are any one of a family of natural hydrated aluminum silicates that they are nonstoichiometric complexes varying a wide range of compositions as solid solutions series. At now, there are about more than 40 morphological types of natural zeolites, the most found in nature of which are mordenite and clinoptilolite (Cl). The value of zeolites is characterized by an open-work aluminosilicate framework with a set of channels and a large cagelike cavities that their dimensions (windows) are large enough for atoms or atomic clusters and ions of most even organic and inorganic molecules to enter into them. The zeolite structures are based on three dimensional frameworks of silicon and aluminum anionites. The aluminosilicate framework of zeolites has a negative charge, which is balanced by the cations of alkali and alkali-earth metals and water molecules connected weakly with the pores and cavities of the framework. Water in the channels can be removed by heating or evacuation of the zeolite without destroying the rigid framework so its structure remains practically the same. The zeolite pores, which connect to each other through “windows”, have a right form of the perforated channel chain within the crystals. All these features of zeolites provided to examine the electron porous emission, electron multiplication and gas discharge in pores, dielectric and electric properties at pore saturation by different gases and liquids, as well as adsorption and ion-exchange phenomena. In Azerbaijan, it is found that 14 types of minerals of the zeolite family associate with magmatism, dating the geological history of Azerbaijan. Geological feature of zeolite areas gives reason to believe that the territory of Azerbaijan is one of

the most promising regions for natural zeolites [1], which are found wide application in many areas.

On the basis of the radiographic and chemical analysis on aluminosilicate-zeolite, it is established that the natural zeolite examined by us is affiliated to zeolites of Cl species [2]. The crystal structure of Cl has a monoclinic cell with the cell dimensions  $a = 17.74\text{ \AA}$ ,  $b = 17.9\text{ \AA}$ ,  $c = 7.4\text{ \AA}$ , with the symmetry space group  $C2/m$ ,  $\beta = 117^\circ$ .

Crystalline structure is composed of a three-dimensional network of silicon and aluminium tetrahedrons which are negative charged, interconnected by nodes with a pore-nanochannels of two types A and B that dimensions  $0.6 \times 0.4\text{ nm}$  - (A type) and  $0.4 \times 0.4\text{ nm}$  - (B type) [3, 4]. These channels are filled with the extra-framework cations that is,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , which compensate the negative charges of the framework and a large number of molecules of  $\text{H}_2\text{O}$ -water, therefore they are mobile and may move to new positions. Water plays a major task in the stability of Cl framework due to influencing interactions between positively charged cations and the negative framework, and supplies extra charge carriers such as  $\text{H}^+$ ,  $\text{OH}^-$ . Hence, it is believed that  $\text{H}_2\text{O}$  molecules cause increasing [5-7], the mobility of ions in the pores space.

Traditionally, the application of zeolites has been limited to using them as ion exchangers to cleaning liquids from impurities. In recent years, the study of physical properties of zeolites is intensified. It is connected with an opportunity to use them as certain elements of the electrical circuits. The main result of these studies is that the replacement of the positive ions in the pores of the zeolites leads to a substantial change in the dielectric spectra and non-linear current-voltage characteristics (CVC) [8]. In

particular, it is found that the CVC consists of two parts: high-ohmic at low voltages and low-ohmic at high voltages. In our work, such CVC is obtained from non-modified (natural) zeolite. However, there are new results in the study of charge transport in zeolite materials. In particular, in our work the CVCs are studied depending on the pressure in the chamber containing natural zeolite. In [9], there has been observed transition from current decreases with time to steady state current at low pressure. These results are obtained for mixtures of the zeolite with silicon powder, the zeolite with copper powders, as well as on the zeolite plate. In the latter case, the current is accompanied by a gas discharge. On the basis of these results it is suggested that using the zeolites with low water vapor content as a cathode in the gas discharge system. This approach allows us to reduce the ignition voltage of the gas discharge with several tens of volts. In [10], the CVCs of the zeolite (clinoptilolite) powder which included 10% of the silicon powder was measured in the chamber at different air pressures. It is found that the steady-state current is observed in a constant electric field, in contrast to pure zeolite powder, where the currents are not stationary and decreases with time. Such a significant effect of a small amount of Si powder on the electrical properties of zeolite powder indicates that such compounds are a promising material for use of such mixtures. In this connection, special urgency needs in the study of the dielectric response of zeolite materials.

Water in the zeolite structure and position of the cations which are located inside zeolite channels, play a dominant role for understanding their dielectric characteristics. The investigation of zeolite in an aqueous state dielectric and absorption characteristics gives an important knowledge about their sorption features and chemical reaction processes [11, 12]. The measurement of zeolite dielectric permittivity is determined the water sorption properties, and the absorbed water molecules in zeolites play a significant role in dielectric behaviors at room temperature [13]. In [14] it has been shown the influence on the dielectric response of the ionic conductivity and two relaxation processes: rotational polarization of adsorbed water molecules and the polarization associated with the accumulation of charges on the boundary of the crystallites and the intercrystalline space. The dielectric relaxation mechanism observed at the intermediate frequencies (that is frequencies below 100 MHz) are associated to the absorbed water molecules in the structure and the displacements of ions (cations) in the large cavities and channels in which regions the cations are localized and where they can migrate between neighboring ionic positions. We also investigated the absorption spectra of natural zeolite-Cl in a wide range of frequencies from  $3600\text{ cm}^{-1}$  to  $100\text{ cm}^{-1}$ . Identified bands caused by the absorption of water in the pores of the zeolite. The observed broad band at a frequency of  $3470\text{ cm}^{-1}$  is caused by vibration of water molecules. The strongest band at a frequency of  $1638\text{ cm}^{-1}$  confirms the high diffusion mobility.

Properties of zeolite structure at where bands changes are occurred, where the water absorption is arisen, and the presence of certain functional groups in a molecule, are

determined with the IR spectra of the Cl. It should be noted that the IR spectra is sensitive to change in both the hydrogen and coordination bonds in the crystal [15], resulting in our interest to the measurement of the absorption of water in Cl in the IR-region. The IR spectrum is a useful technique for the quantitative determination the characteristic of Cl and the vibrations into the structure [16, 17]. IR spectra of zeolites provide obtaining information about their hydration processes, the state of water, and the existence of hydroxyl groups and the localization of cations. The IR of Cl shows that depending on the radius, atomic number and valence of the exchange cations, change in the position of maxima and the intensities of high frequency bands takes place in the range of  $400\text{ to }4000\text{ cm}^{-1}$  [18, 19].

Under various conditions a number of works is devoted to study on dielectric spectra of zeolites. The dielectric spectra may overlap extremely wide ranges of frequency ( $10^6\text{--}10^{12}\text{ Hz}$ ), temperature ( $-170\text{ }^\circ\text{C}$  to  $+500\text{ }^\circ\text{C}$ ), and pressure [20 - 22]. In refs [23, 24] revealed that the dependence of dielectric properties of the zeolite is based on the type of the primary ion, i.e. an ion which controlled the ion-ion migration polarization. In this work, we studied the temperature dependence of dielectric permittivity at various frequencies. It is found that the experimental results are satisfactorily described by a model of two-componential zeolite-air pores system. It should be noted that in this work before experiment the water removed by evacuation or annealing from pores of the framework. Influence of water on dielectric properties of zeolites is studied in ref [25]. In this study, the natural zeolite Ca-Cl was investigated. It has been studied that the dielectric spectra caused by waters relaxation (at its various concentration) in the Cl - water system. It is established that the contribution to dielectric properties of zeolite water connected in the zeolite pores and waters in free volume is distinguished. It is shown that the humidity which is less than 12 percent all the water is in a bound state. In ref [18] it is established that the modification of some ions increase the dielectric permittivity with respect to the original sample while others reduces. As follows from the review of the dielectric properties of Cl was studied in limiting cases. In ref [1] the properties of dehydrated Cl were studied and in work ref [2] specifically hydrated sample of Cl were studied. Besides in ref [26], it is found out that two relaxation processes and one conductivity contribution have been occur for several pure zeolite powders, FAU, and LTA, under microwave frequencies range. In this study, the effect of the hydration level has also been studied and it is found that water loading particularly affects charge carriers mobility and the conductivity is improved by cation solvation by water molecules.

However, instead of above the consequences of any one of the many parameters defining the dielectric relaxation processes, we shall try to focus on some remarkable common features and draw conclusions from them. Therefore, we are intended to give an overview of dielectric relaxation processes with the high density (natural plate) and low density (unpressed powder) which

has a much greater surface area contact with water despite the evident lack of proper understanding of the concentration of these complexes on the dielectric spectra. In this case, measurements are carried out with two objects: a plate of natural CI and unpressed CI powder. For this reason, we study the intermediate frequencies ranges which occur in this range a sharp change, differently from in the microwave or infrared region which is effective in the high-frequency domain.

In this work, we study the dependence of the dielectric properties of zeolites on the type of the basic ion and we devoted to find a correlation between these properties and chemically induced structural modifications. The aim of this work is to study the intermediate case (the intermediate frequencies that below 100 MHz) of the dielectric relaxation and conduction phenomena compared with a wide medium for the first time to our knowledge. That is, the measurement of the dielectric spectrum in an air and not at very high vacuum ( $10^{-2}$  Torr) in this study. Our other goal is the combined influence of water vapor content in the CI and its density. At the same time, we proposed to reveal structural properties of CI with the IR spectra.

## 2. Experimental

### 2.1. Materials

The object of the study was to used natural zeolite which is a CI with a low water vapor content: crystal system - monoclinic, space symmetry group C2/m, the unit cell parameters:  $a = 1.761$  nm,  $b = 1.780$  nm,  $c = 0.741$  nm,  $\beta = 115.2^\circ$ , the chemical composition confirmed by X-ray diffraction carried out by us [2] which was following the analysis that containing  $\text{Al}_2\text{O}_3$  - 11.36%,  $\text{SiO}_2$  - 67.84%,  $\text{Na}_2\text{O}$  - 1.25 %,  $\text{MgO}$  - 0.49%,  $\text{P}_2\text{O}_5$  - 0.11%,  $\text{SO}_3$  - 0.03%,  $\text{K}_2\text{O}$  - 3.01%,  $\text{CaO}$  - 0.29%,  $\text{TiO}_2$  - 0.08%,  $\text{MnO}$  - 0.078%,  $\text{Fe}_2\text{O}_3$  - 1.19%,  $\text{KJ}$  - 11.64. The monoblock, formed in the bowels of the earth, cut bars, which after machining became parallel-plane plates.

Natural zeolite powder obtained by grinding in a mortar pieces, and then processing them in a planetary mill type FRITSCH, where they were brought to the powder state with a particle sizes of 0.1  $\mu\text{m}$ . The planetary P4 vario ball mill is the Fritsch commercialized version of the G5 prototype.

### 2.2. Measurement method

For the measurement, the samples were placed in a cell between two planar electrodes, one of which is a semi-transparent conductive  $\text{SnO}_2$  layer on a glass disk and the other is a polished metallic Cu disk. By using the spanner nuts copper disk, powder is compressed in a cell which is a layer with a thickness of 2 mm and a powder or plate with diameter of 1 cm. The cell was placed in a chamber equipped with windows for visual observation and recording of the discharge, electrical input, and output to pump gas from the chamber. The residual pressure in a

chamber was recorded by digital manometer and the pressure was changed from atmospheric pressure to  $10^{-2}$  Torr, and the cell connected to the E7-20 LCR meter (impedance, resistance and capacitance) in the frequency range 25 Hz - 1 MHz. Measurements were performed at room temperature and 85% air humidity. The spectra are taken on Varian-3600 FT-IR spectrophotometer in the frequency interval of average ( $4000$  up to  $400$   $\text{cm}^{-1}$ ) of IR region.

## 3. Results

### 3.1. Dielectric spectrum

The capacitance C and the resistance R are measured by E7-20 LRC meter and the values of real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of dielectric permittivity are calculated according to ref [15]. The typical spectra of the dielectric permittivity associated with the relaxation of water molecules of the adsorptive layer for the studied porous zeolites versus frequency are displayed in Fig. 1 and 2. Table 1 show that these values depend on the frequency of plate and powder in the air and vacuum conditions. Fig. 1 and 2 shows that the dependence of frequency on real and imaginary parts of dielectric permittivity of these samples. Here  $\epsilon'$  - the real part of the dielectric permittivity;  $\epsilon''$  - the imaginary part of dielectric permittivity. From the Figs. 1, 2 and Table 1, it shows that both the dielectric permittivities are greater in an air than a vacuum for all frequencies. For the real and imaginary parts of the dielectric permittivity we have used the following simple formulas, which are based on the model of a relaxation oscillator (simulates the ionic polarization) with the relaxation time  $\tau$  [15]:

$$\epsilon_i' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega\tau)^2} \quad \epsilon_i'' = \frac{(\epsilon_s - \epsilon_\infty)\omega_i\tau}{1 + (\omega_i\tau)^2} \quad (1)$$

Here  $\epsilon_s$  - static dielectric permittivity,  $\epsilon_\infty$  - high-frequency dielectric permittivity. Using the data given in Table 1 (lines 1-17), we have calculated a relaxation time  $\tau$  for all cases with the formulas (1). To calculate the relaxation time  $\tau$  from  $\epsilon'$ , the experimental data are divided into groups included only three points. For each of groups  $\tau$  value was determined. Specifically, from three experimental points the system with three equations with the three unknown -  $\epsilon_\infty$ ,  $(\epsilon_s - \epsilon_\infty)$  and  $\tau$  is formed:

$$\epsilon_i' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega_i\tau)^2} \quad i = 1, 2, 3. \quad (2)$$

where  $\omega_i$  are the frequencies at which measurements were performed, and the  $\varepsilon'_i$  - corresponding to them measured values of the real part of the permittivity given in Table 1. From the formula (2)  $\varepsilon'$  and  $(\varepsilon_s - \varepsilon_\infty)$  can be excluded, and  $\tau$  can be expressed in terms of frequency and dielectric constants:

$$\tau = \frac{\varepsilon'_1(\omega_2^2 - \omega_3^2) + \varepsilon'_2(\omega_3^2 - \omega_1^2) + \varepsilon'_3(\omega_1^2 - \omega_2^2)}{\omega_1^2\omega_2^2(\varepsilon'_2 - \varepsilon'_1) + \omega_3^2\omega_1^2(\varepsilon'_1 - \varepsilon'_3) + \omega_2^2\omega_3^2(\varepsilon'_3 - \varepsilon'_2)} \quad (3)$$

The same operation is applied for calculation the  $\varepsilon''$ , but in this case the experimental data are divided into groups of two points. Specifically, from two experimental points the system two equations with two unknowns  $(\varepsilon_s - \varepsilon_\infty)$ ,  $\tau$  is formed.

$$\varepsilon''_i = \frac{(\varepsilon_s - \varepsilon_\infty)\omega_i\tau}{1 + (\omega_i\tau)^2}, \quad i = 1, 2. \quad (4)$$

where  $\omega_i$  - the frequency at which the measurements were conducted, and  $\varepsilon''_i$  - corresponding to them measured values of the imaginary part of the permittivity given in Table 1. From the formula (3),  $(\varepsilon_s - \varepsilon_\infty)$  can be excluded, and  $\tau$  expressed in terms of frequency and dielectric constants

$$\tau = \frac{\varepsilon''_1\omega_2 - \varepsilon''_2\omega_1}{\omega_1\omega_2(\varepsilon''_2\omega_2 - \varepsilon''_1\omega_1)} \quad (5)$$

It should be noted that, in this approach, from N experimental points  $\tau$  can be calculated  $N!/(3!(N-3)!)$  times (the number of combinations of N elements by 3) from measurement of the real part of the permittivity  $\varepsilon'$  and  $N!/(2!(N-2)!)$  times (the number of combinations of N elements by 2) from measurement of the imaginary part of the permittivity  $\varepsilon''$ .

### 3.2. FTIR spectrum

To reveal how the water is bound to the natural Cl, where bands the modification occurs, the presence of certain functional groups in a molecule, and what is reason for higher sorption of positive metal ions the IR spectra of the Cl was examined. For a better interpretation the absorption spectrum of the Cl, it is necessary to characterize its properties. Interpretation of the spectrum is based on assignment of the IR bands to certain structural groups in the various frameworks [27]. It is also possible

to characterize zeolite systems other than adsorption and desorption of water by IR. The comparative surface characterization of natural zeolites has been investigated by FT-IR spectroscopy. The spectra are taken on Varian-3600 FT-IR spectrophotometer in the frequency interval of average (4000 up to 400  $\text{cm}^{-1}$ ) IR region.

The two wide absorption bands: from 3400 up to 3500  $\text{cm}^{-1}$  and wide band from 1000 up to 1060  $\text{cm}^{-1}$  are clearly expressed on spectrogram (Figure 4) taken in frequency interval 3500 up to 400  $\text{cm}^{-1}$ . The frequency 3470  $\text{cm}^{-1}$  shows on the presence of coordinating water and its large width evidences on localization of (OH) groups in the channels connected with each other by hydrogen bonds. At investigation of IR zeolite absorption spectra it is necessary to note that all observable absorption bands relate to two oscillation types: - 1 are oscillations inside  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedrons being the primary structural units not reflecting the peculiarities of zeolite structure; - 2 are oscillations on tetrahedron external bonds.

The more strong absorption bands observed in spectra of all zeolites at 1250-950  $\text{cm}^{-1}$ , frequency is 1053  $\text{cm}^{-1}$  belonging to this interval is caused by oscillations (T-O<sub>i</sub>) inside tetrahedrons and is related to first type oscillation, i.e. isn't sensitive to zeolite structure. The frequency 1638  $\text{cm}^{-1}$  can be related to deformation oscillations H-O-H relating to second type oscillations, i.e. is sensitive to zeolite structure; the frequency 796  $\text{cm}^{-1}$  is caused by symmetrical valence oscillations inside tetrahedrons (T-O<sub>i</sub>), i.e. is related to first type oscillations; the frequency 461  $\text{cm}^{-1}$  is related to deformation valence oscillation inside tetrahedrons and also belongs to first type oscillation; the frequency 605  $\text{cm}^{-1}$  is responsible for oscillations of duplex rings and depends on connection character of tetrahedrons which form the nanochannel inlets.

### 4. Discussion

Fig. 1 and 2 shows the frequency variation of dielectric permittivity ( $\varepsilon'$  and  $\varepsilon''$ ) for two samples of Cl with 85% air humidity at the room temperature in the at  $10^{-2}$  Torr and atmospheric pressure. It was observed from the figures that the values of dielectric permittivity were found to be rapidly decreasing with an increasing frequency. For all samples, with an increase of electric field frequency from 20 Hz to 1 MHz, the dielectric constant  $\varepsilon'$  decreases by more than two orders of magnitude. It is noteworthy that the similar frequency dependence of dielectric loss  $\varepsilon''$  was observed for all samples. Similar results were found for natural Cl in ref. [10, 14]. The dielectric losses factor  $\varepsilon''$  is characterizing the value of energy loss of the electric dipole in the electric field.

The influence of polarization is importantly observed at atmospheric pressure in comparison with low pressure. This  $\varepsilon''$  behavior was found in the frequencies range from  $10^4$  to  $10^6$  Hz for atmospheric air as it can be seen in Fig. 2. The polarization peak appeared at these frequencies range. With increasing pressure the maximum is shifted to the higher frequencies. These maxima are related to the

dielectric relaxation phenomena for which wavelength interacts with the zeolite is affected by the structure and nature of the zeolite. The increase of the dielectric losses is more significant in the low frequency range. This increase of losses can probably be attributed to a conductivity phenomenon consequence of cations hopping diffusion along zeolite structure [5, 25] and the relaxation properties of zeolites [14, 23]. In such a case, the chemical composition of the zeolite with respect to the proportion of Si/Al, properties of the exchanged cations, the contents of the water vapor content, and the temperature of the sample [5] are influenced the conductivity and the relaxation properties of zeolites. Such loss has been frequently observed in zeolites and has been supposed to due to dc ionic conductivity loss and a grain boundary effect [29].

Dipolar relaxations and ionic conductivity are clearly coexisting mechanisms that govern the evolution of dielectric properties over the frequency range.

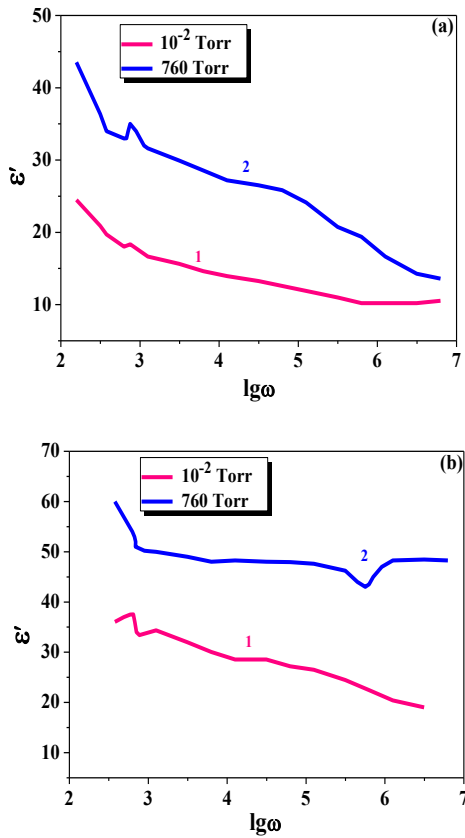


Fig. 1. Frequency dependence of real dielectric permittivity for (a) Cl powder and (b) plate at different experimental conditions: Curve 1 - at  $10^{-2}$  Torr, curve 2 - at 760 Torr pressure.

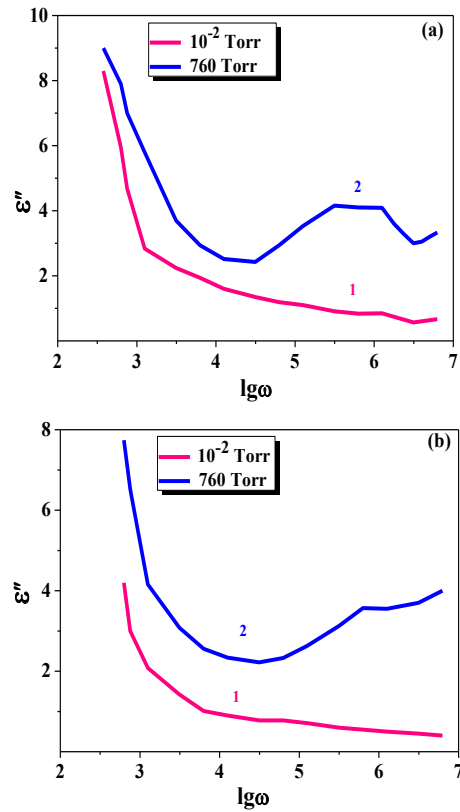


Fig. 2. Frequency dependence of on imaginary dielectric permittivity for (a) Cl powder and (b) plate at different experimental conditions: Curve 1 - at  $10^{-2}$  Torr, curve 2 - at 760 Torr pressure.

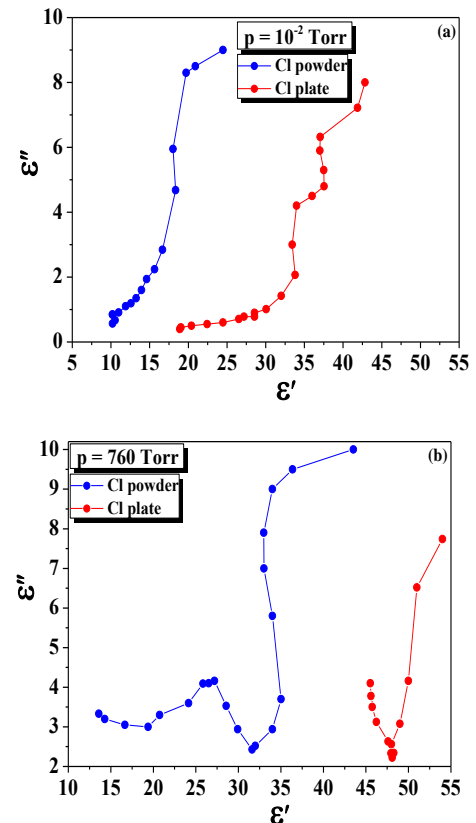


Fig. 3 Argand diagrams of clinoptilolite powder and plate (a) at  $10^{-2}$  Torr, and (b) at 760 Torr pressure.

Table 1. Values of dielectric permittivities and frequency of Cl plate and powder measured from  $10^{-2}$  Torr to 760 Torr.

Frequency $\omega/2\pi$	Cl Plate				Cl Powder			
	$\epsilon'$		$\epsilon''$		$\epsilon'$		$\epsilon''$	
	$10^{-2}$ Torr	760 Torr	$10^{-2}$ Torr	760 Torr	$10^{-2}$ Torr	760 Torr	$10^{-2}$ Torr	760 Torr
25	42.84	53.00	8.00	8.55	24.48	43.52	9.00	10.00
50	37.04	55.00	6.32	8.15	20.90	36.38	8.50	9.50
60	36.04	60.00	4.80	8.00	19.72	34.00	8.30	9.00
100	38.00	54.00	4.20	7.74	18.02	32.98	5.95	7.90
120	33.22	50.00	3.00	6.52	18.36	35.02	4.68	7.00
200	34.68	50.00	2.08	4.16	16.66	31.62	2.84	5.80
500	32.00	49.00	1.42	3.08	15.64	29.92	2.24	3.70
$10^3$	30.06	48.00	1.01	2.56	14.62	28.56	1.94	2.94
$2 \times 10^3$	28.56	48.28	0.9	2.34	13.94	27.20	1.60	2.52
$5 \times 10^3$	28.56	48.00	0.78	2.22	13.26	26.52	1.35	2.43
$10^4$	27.02	47.94	0.78	2.33	12.58	25.84	1.19	2.94
$2 \times 10^4$	26.52	47.60	0.71	2.63	11.90	24.14	1.10	3.53
$5 \times 10^4$	24.48	46.24	0.60	3.125	11.00	20.74	0.91	4.16
$10^5$	22.44	43.52	0.55	3.57	10.20	19.38	0.84	4.10
$2 \times 10^5$	20.4	48.28	0.50	3.55	10.20	16.66	0.85	4.09
$5 \times 10^5$	19.04	48.46	0.45	3.70	10.20	14.28	0.57	2.86
$10^6$	18.90	48.28	0.4	4.00	10.54	13.60	0.67	3.33
	$\tau = 3 \times 10^{-5}$ s	$\tau = 1 \times 10^{-5}$ s	$\tau = 2 \times 10^{-5}$ s	$\tau = 1 \times 10^{-5}$ s	$\tau = 0.6 \times 10^{-5}$ s	$\tau = 0.5 \times 10^{-5}$ s	$\tau = 2 \times 10^{-5}$ s	$\tau = 0.8 \times 10^{-5}$ s

They are affected by a number of factors linked to the zeolite properties, the importance of which has to be examined. 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 [30]. When it is evaluated with a frequency of 2 - 7 MHz, imaginary dielectric permittivity  $\epsilon''$ , also called dielectric loss, of Cl were seen the peaks in the range of 10 - 4 and 23.8 - 3.33 values for plate and powder respectively, at room temperature and at atmospheric pressure. At a maximum frequency, the dielectric loss is 4 MHz, namely relaxation frequency, and the relaxation time of the plate and the powder are  $1 \times 10^{-5}$  s, and  $0.8 \times 10^{-5}$  s, respectively. As the frequency increases, when approaching the relaxation region, the dielectric loss increases and dielectric permittivity  $\epsilon''$  rapidly decreases. Since there was no polarization at this region, there wasn't the dielectric loss. The reason of the rapid decrease of the dielectric permittivity  $\epsilon''$  is the relaxation frequency. Indeed, the reason of the declining the imaginary dielectric permittivity  $\epsilon''$  is that the electrical conductivity is raised because of the ions which are bond loosely to the structure, are accompanied with the conductivity at the high temperature, that is room temperature. At the same time, absorption water increases the conductivity of the Cl with the ions in the structure and leads to decreasing the

value of  $\epsilon''$ . These results indicate the existence of relaxation processes. In hydrated Cl at atmospheric pressure, Fig. 2a and 2b, one or two relaxation phenomena seem obvious for materials. Powder Cl have the lowest complex permittivities contrasting with plate Cl, which have a much greater surface area contact with water and higher permittivities. At hydrated Cl in Figure 2a and 2b, dielectric losses increase drastically, and a conductivity phenomenon is qualitatively detected by a strong increase in the real and imaginary parts corresponding to the low frequency scale for major ionic Cl. This phenomenon is evident that the water molecules are adsorbed, and the relaxation frequency is due to the rotational polarization of adsorbed water which is seen at atmospheric pressure, depending on the zeolite nature. At an intermediate frequency, this relaxation is the consequence of existing interaction which takes place between water and the exchangeable cations and the oxygen atoms of the framework, and between neighboring molecules of water (hydrogen bound). This relaxation frequency value is in a common order of magnitude for bound water molecules [26]. Our results are coherent with the literature [14, 26].

To investigate the influence of density and water vapor content on the dielectric response of natural zeolites, we have used the average relaxation time. As in all cases the relaxation time is identical only up to the order, and then of course it shows essential variation of the relaxation times. In this regard, the data for all samples, at  $10^{-2}$  Torr

and at 760 Torr are plotted on Argand diagrams in Figure 3a and b, respectively, showing the relationship between  $\epsilon'$  and  $\epsilon''$ . However, our attempts are to carry out the analysis using the diagrams of Cole-Cole which has proved unsuccessful (see Figs. 3a and b). The same analysis is reported in [14]. To understand why so it has turned out, we shall consider some features of ion-conductive porous zeolites in comparison with single-phase mediums. The complexity and the relationship between the electric characteristics of such a complex objects are not simply from formal transformation of Maxwell's equations for the total current, and are caused by the physical peculiarities of the flow in these processes of conductivity and polarization. It should be noted that the classical consideration of the conduction current and displacement current are accepted for an ideal conductor and dielectric, is not applicable to zeolites with ionic conductivity and the developed pores systems. In such a complex heterogeneous mediums, the conduction current as directed the translational motion of the charge carriers and the displacement current as vibrational displacement of the bounded charges should have additional phase shifts with respect to strength  $E$  of an external alternating field, since in porous material there are no ideal free and ideal bounded charge carriers. These carriers (ions, groups and complexes) can be called as semi-free depending on energy structure of the pore space. In the various (at the mesoscopic scale) areas of such a material the energy spectrum of charged particles is different. Because of such inhomogeneity, additional phase shifts of the conduction current and displacement current should be various for different frequencies of the external field. Hence it should be note that the static and high-frequency dielectric permittivity as electrical characteristics of the heterogeneous mediums should not be constants, but can be complex functions of frequency. Therefore, we have used this method for analysis of the dielectric response, which allowed determining the relaxation time of local frequency. Spread of the relaxation time on frequencies was indeed really significant. However, after averaging on the spectrum of the relaxation time was approximately the same at different water vapor content and density of natural zeolite. It also has proved our approach.

To explain the results, we will proceed from the notion of polarization which the polarization effects are visible in the frequency dependence of imaginary part of complex permittivity  $\epsilon''$  creating one or more peaks, related to the following types of conductivity: 1. The conductivity of the positive ions in the zeolite pores, mobility of which is increased due to the interaction with molecules. 2. The conductivity of the positive ions is reduced due to increase of scattering in their energy at atmospheric pressure; 3. The conductivity of water located in the intercrystalline space.

From the analysis of the experiment (1-6), the overall trend of influence of air pressure is to increase both the real and imaginary parts of the dielectric permittivity. We attributed to this increasing mobility of ions in the pores due to their interactions with water molecules. It is important that the relaxation time  $\tau$  is different in all

cases but this difference is not more than one degree. Hence we conclude that both object of relaxation and its mechanism of relaxation in an alternating field are the same in all these cases. Then the difference of the real and imaginary parts of the dielectric permittivity in these cases (i.e. plate - powder; vacuum - air) should be explained by changing at concentration of relaxation oscillators. Specifically, we believe that the main contribution to the observed phenomenon makes a positive ion in the pore of zeolite is associated with a water molecule. The vacuum in our experiment is not high. Therefore, we may assume that the number of ions associated with the water in this case is sufficient to explain the observed values of the real and imaginary parts of the dielectric permittivity. The transition from air to the vacuum of such water-related ions increases by an increment of both dielectric permittivities. The increase in the real and imaginary parts of the dielectric permittivity of powder compared with the plate is associated with an increase in the intercrystalline space, which is filled with water. The fact is that in unpressed powder, each zeolite crystal has a much greater surface area contact with water than the same crystals in the natural plate [31].

The identification of absorption bands in the spectral interval from  $600\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$  was determined with high resolution spectrogram (see Fig. 5). It is emphasized that  $1558\text{ cm}^{-1}$  band relating to deformation oscillations of H-O-H group depends on zeolite structure and sensitive to its changes. At the same time, the  $875\text{ cm}^{-1}$ ,  $778\text{ cm}^{-1}$ ,  $713\text{ cm}^{-1}$ ,  $694\text{ cm}^{-1}$ ,  $668\text{ cm}^{-1}$  bands which can be related to symmetrical valence oscillations inside tetrahedrons (T-O<sub>i</sub>) are identified.

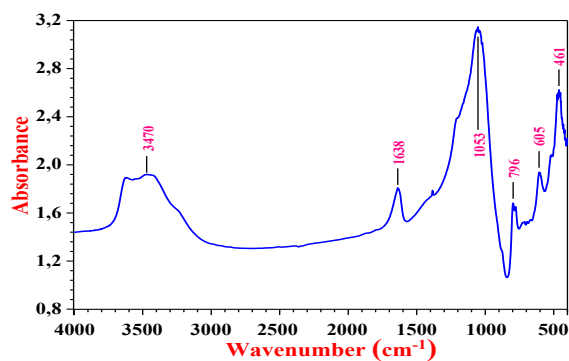


Fig. 4. The absorption spectrum of natural clinoptilolite in the mid-IR region.

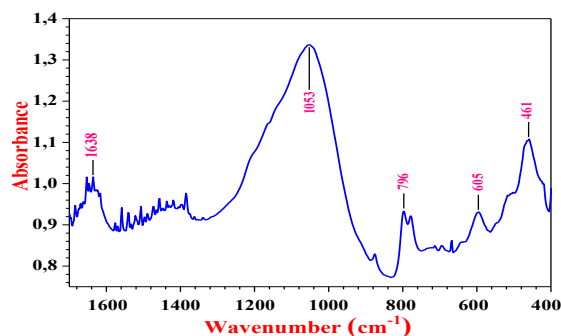


Fig. 5. The absorption band of natural clinoptilolite.

#### 4. Conclusions

Thus, in the present study it is established that the reduction in the density of the crystallites leads to an increase the influence of water vapor content on the dielectric spectra. The fact that in our experiments was not detected a significant changing in the relaxation time demonstrated the crucial role of the interaction of water molecules with positive ions in the pores. In other words, the mechanism of polarization determined by the dielectric spectra (movement in an electric field of positive ions associated with molecules of water) remains the same in all these cases (air - vacuum, plate - powder). The changing of the spectra in all cases is associated with water into the pores of the zeolite. It should be noted that in the same way it is possible for different ion-substituted analogues samples to determine the extent of the interaction between positive ions in the pores with water molecules. FTIR studies indicated that the band, which is formed due to the interactions of water molecules with the framework via hydrogen bonds, the presence of coordinating water (at  $3470\text{ cm}^{-1}$ ) and localization of (OH) groups in the channels. All values of absorption bands observed by us in IR-spectra are in good agreement with literature data [32], on IR-spectra of high-siliceous compounds.

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