The Dielectric Permittivity of Natural Clinoptilolite In The Wide Range of Frequencies

A. X. Muradov
Institute for Physical Problems
Baku State University, Z.Khalilov str., 23, Baku AZ 1148, Azerbaijan

V. I. Orbuch
Institute for Physical Problems
Baku State University, Z.Khalilov str., 23, Baku AZ 1148, Azerbaijan

G. M. Eyvazova
Nanoresearch centre
Baku State University, Z.Khalilov str., 23, Baku AZ 1148, Azerbaijan

N. N. Lebedeva
Institute for Physical Problems
Baku State University, Z.Khalilov str., 23, Baku AZ 1148, Azerbaijan

Ch. G. Akhundov
Institute for Physical Problems
Baku State University, Z.Khalilov str., 23, Baku AZ 1148, Azerbaijan

A. M. Mamedov (Corresponding author)
Nanotechnology Research Center (NANOTAM), Bilkent University, 06800 Bilkent, Ankara, Turkey
International Scientific Center, Baku State University, Baku, Azerbaijcan
E-mail:mamedov@bilkent.edu.tr

Abstract
The dielectric permittivity of natural clinoptilolite has been measured in the wide frequency range up to microwave frequencies ($4,5 \cdot 10^{10}$ radn /s) It describes in detail the method of measurements of the real part of dielectric permittivity by means of partly filled rectangle waveguide. Obtained result of $\varepsilon^1 = 1,53$ complements the results obtained previously in the range up to 10^6 Hz and makes it possible to interpret the frequency dependence of the dielectric permittivity with the help of the model of relaxation oscillator.

Keywords*: natural zeolite, clinoptilolite, the dielectric permittivity, microwave frequencies, partly filled rectangular waveguide.

1. Introduction

Zeolites, a large group of natural hydrated aluminum silicates, are nonstoichiometric compounds, the compositions of which vary widely forming series of solid solutions. The value of zeolites caused by an openwork alumino silicate framework with a set of channels and cavities, the dimensions of input "windows" of which are large enough for molecules and ions of most organic and inorganic compounds to enter into them. The zeolite frameworks are formed from silicon and aluminum antimonity. It has a negative charge, which is compensated by cations of alkali and alkaline earth metals and water molecules occupying pores and cavities in the framework and weakly bound with it. Water may be removed by heating the zeolite or air evacuation from it. This does not influence the framework: its structure remains almost unchanged. The zeolite pores, which connect to each otherthrough "windows", have a right form of the perforate channel chains within the crystals. That is why the zeolites can be treated as the objects on which besides well-known phenomena (absorption, ion-exchange phenomenon) can investigate the

electron porous emission, electron multiplication and gas discharge in pores, dielectric and electric properties at pore saturation by different gases and liquids. Based on X-ray diffraction data and spectral chemical analysis, we determined that the natural zeolite studied in this work can be classified as high-silica zeolite of the clinoptilolite type [1]. The crystal structure of clinoptilolite belongs to the monoclinic syngony with lattice parameters a= 17,74 Å, b= 17,9 Å, c=7,4Å and its space group is C2/m with β= 117 °.

Crystalline structure is composed of a three –dimensional network of silicon SiO_4 and aluminumAlO_4 tetrahedrons which are negative charged, interconnected by nodes with pore- nanochannels of two types A and B, that dimensions 0,6x0,4nm- A type and 0,4x0,4nm- B type. These channels are filled with extra-framework cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, which compensate the negative charge of the frame, and a large number of molecules of H_2O-coordinating water. Water plays an important role for the stability of clinoptilolite framework. Between the oxygen atoms from the framework, which is being coordination of positively charged ions, and H_2O molecules, located in the coordination of cations, the hydrogen bonds form. It, as believed [2-4], leads to increase in mobility of ions in pores space.

A number of works is devoted to study on dielectric spectra of zeolites under various conditions. In ref. [5] revealed that the dependence of dielectric properties of zeolite is based on the type of the primary ion, i.e. an ion which controlled the ion-ion migration polarization. It is established that the modification of some ions increases the dielectric permittivity with respect to the original sample while others reduce. The temperature dependence of dielectric permittivity at various frequencies was studied in the work. It is found that the experimental results are satisfactorily described by a model of two- component 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 was studied in ref. [6]. The natural zeolite Ca-clinoptilolite was investigated in this study. It has been studied that the dielectric spectra caused by water relaxation (at its various concentration) in the clinoptilolite-water system. It was found that the contribution to dielectric properties of zeolite water connected in the zeolite pores and water in free volume is distinguished. It is shown at that the humidity less than 12 percent all the water is in a bound state.

In ref. [7] dielectric spectra of natural zeolite (clinoptilolite) are studied in a wide range of pressure from 10^{-1}Tor (vacuum) to atmospheric pressure. The measurements were carried out on samples of high density (natural plate) and low density (unpressed powder) in a frequency range from 20 to 10^6 Hz.

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 Differences in the corresponding dielectric spectra are related to the concentration of these complexes.

In the given work the dielectric permittivity of natural clinoptilolite has been measured in the microwave frequency range. The detailed description of the method of measurements of the real part of the dielectric permittivity by means of a partly filled rectangle waveguide is given. Obtained results of ε¹ completes the results obtained previously in the range up to 10^6 Hz and allows us to apply the developed in [8] method of relaxation oscillator for an explanation of the frequency dependence of the dielectric permittivity.

2. Results and Discussion
2.1 The results of measuring the dielectric spectra using the digital LCR meter
The object of investigation was used the natural zeolite- clinoptilolite. Crystal system- monoclinic, space symmetry group C2/m, the unit cell parameters: a= 1,761 nm, b= 1,780 nm, c= 0,741 nm, β= 115,2°; the chemical composition confirmed by X-ray diffraction carried out by us which was following the analysis that containing Al_2O_3- 11,36% ; SiO_2- 67,84% ; Na_2O- 1,25% ; MgO- 0,49% ; P_2O_5- 0,11% ; SO_3- 0,03%; K_2O- 3,01% ; CaO- 0.29% ; TiO_2- 0.08% ; MnO- 0,078% ; Fe_2O_3- 1,19% ; KJ- 11,64% .The monoblock, formed in the bowels of the earth, cut bars, which after machining became parallel-plane states. For the measurement, the samples were placed in a cell between two planar electrodes, one of which is a semi-transparent conductive SnO_2 layer on a glass disk and the other is a polished metallic Cu disk. 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% of air humidity.

The value of real part of dielectric permittivity (ε^i) has been calculated according to [8] of the capacitance C and the resistance R measured by E7-20 LRC meter.

With increasing frequency ε^i decreases. This decline follows a simple model of a relaxation oscillator and is calculated as follows:

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

where ε_s- static, ε_∞-high frequency dielectric permittivity. Using experimental data was calculated relaxation time $\tau = 10^{-5}$s.

2.2 By measuring the dielectric permittivity by using a partly filled rectangular waveguide

The dielectric permittivity has been measured by short-circuited line method. This method is widely distributed at the dielectric permittivity measurements of materials, as in many practical cases is simpler and versatile in preparing and carrying out the experiment in comparison with other methods.

The sample of material is placed in a short-circuited line segment that is attached to the measuring line (fig.1). The sample should fit snugly to the shorted end of the line segment. In general, a sample length can be arbitrary. However, the measurement accuracy increases significantly if a sample length is a quarter or a half wavelength in the short-circuited line segment with a dielectric.
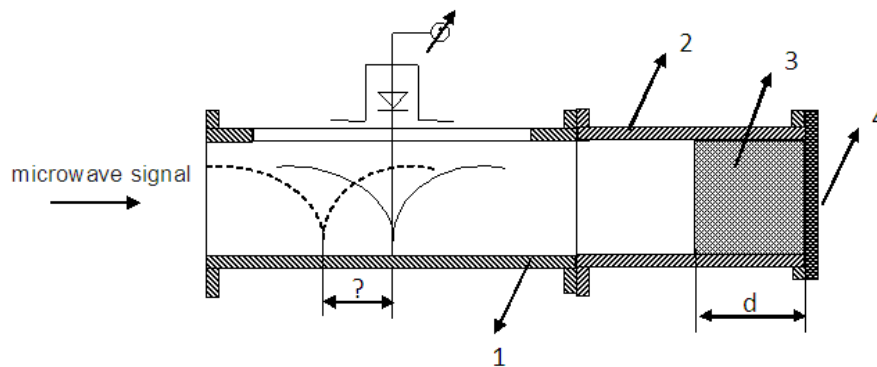

Fig. 1 The arrangement of the dielectric sample in the waveguide line
1-measuring line; 2- waveguide section; 3- the dielectric sample; 4-contactor

In general, the sequence of operations was as follows. The input impedance Z_ε of a short-circuited line segment with the sample is determined on the basis of measurements of minimum position l_{min} and the value of the standing wave ratio. Thereafter, at a known length of a sample d, at a known wavelength λ of a waveguide filled with air, the propagation constant $\gamma = \alpha + j\beta$ is calculated for the short-circuited line segment filled with a dielectric.

Loss tangent $\tan\delta$ and permittivity ε are calculated by a known propagation constant, the wavelength in free space λ_0 for a given operation frequency and critical wavelength in the waveguide λ_{cr}. ($\lambda_{cr}=\infty$ in coaxial).

In the absence of losses (*tan δ=0*), the wavelength in a waveguide filled with a dielectric is given by

$$\lambda_\varepsilon = \frac{\lambda_0}{\sqrt{\varepsilon - \left(\frac{\lambda_0}{\lambda_{KP}}\right)^2}},$$

Here, λ_0 -the wavelength in a free space; $\lambda_{cr}= 2a$ - critical wavelength in the waveguide; a - the width of the wide wall of the waveguide. The phase constant is given by $\beta=2\pi/\lambda$.

Using the ratio for λ_b, β and $\frac{1}{\lambda_0^2} = \frac{1}{\lambda^2} + \frac{1}{\lambda_{KP}^2}$, where λ- the wavelength in the waveguide, we obtain

$$\frac{tg(\beta d)}{\beta d} = \frac{\lambda_6 tg \frac{2\pi \chi_0}{\lambda_6}}{2\pi d} \tag{1}$$

where d is the thickness of the sample, λ_b - the wavelength, χ_0 - the distance from the front of the sample to the first minimum, i.e.

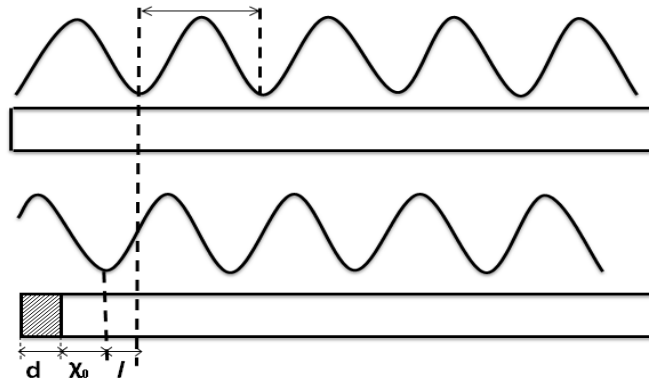$$\chi_0 = \frac{\lambda_b}{2} - l - d \tag{2}$$

Fig. 2 The field distribution in the short-circuited waveguide without the sample and with the dielectric sample

In the right part of formula (1) are the values obtained from the above experiment, where *2π* is taken in radians. After evaluating the relation for the tangent from the table, we determine the value of the tangent. Using this found value of tan we determine the value of the left side of the equation (1). Then on the found value of the left side of the (1) we define the product $\beta \cdot d$ using the table of function *tgx / x*. The unknown quantity *β* find by dividing the product $\beta \cdot d$ by the thickness of the sample *d*. The dielectric permittivity of the investigated sample is determined by the following formula

$$\varepsilon = \frac{1 + \left(\frac{\beta \lambda_{KP}}{2\pi}\right)^2}{1 + \left(\frac{\lambda_{KP}}{\lambda_b}\right)^2} \tag{3}$$

Where λ_{cr} is the length of the critical or the limit wave depending on the size of the waveguide. Table 1 shows the values we measured and determined from tables. It also gives the value of $\varepsilon^{\prime}$ obtained for natural plate in the air at a frequency of $4,5 \cdot 10^{10}$ radn /s. Fig.3 shows the frequency dependence of the real part of dielectric permittivity of the sample.

Table 1.A data table for calculating the value of έ

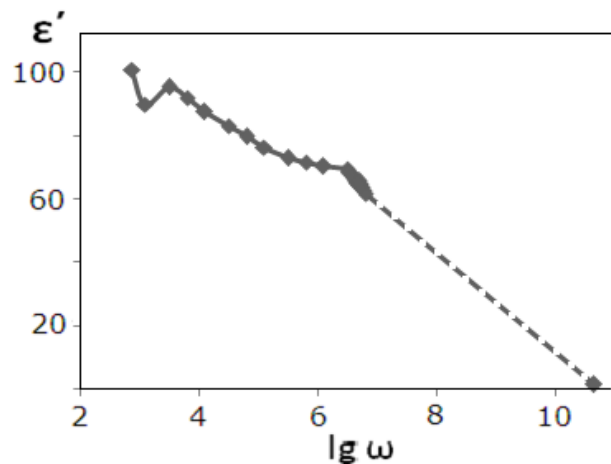| λ mm	l mm	d mm	χ_0 mm	$\lambda_{кр}$ mm	tgβd/βd	βd	β	έ
40	1.5	7.7	10.8	46	-6.29	1.67	0.217	1.53

Fig.3 The frequency dependence of the real part of the dielectric
permittivity of the sample in air at atmospheric pressure

As shown in Fig., the dependence of the dielectric permittivity on the logarithm of the frequency in the range 10^2-10^6 radn /s is close to a straight line. We continued this line up $\omega=10^{10}$ radn /s, thus approximating the frequency dependence in the range 10^6-10^{10} radn /s. It turned out that the point corresponding to this measure is almost on an approximation straight line. This fact gives a reason to believe that such an approximation is close to reality.

3. Conclusion

The dielectric permittivity of natural zeolite-clinoptilolite has been measured in the wide frequency range up to microwave frequencies ($4,5 \cdot 10^{10}$ radn /s). In a frequency range from 200 to 10^6 Hz, we used the method of impedance spectroscopy when a sample in a sandwich geometry connected to the input of the device E7-20 LCR meter.

In the microwave frequency range ($4,5 \cdot 10^{10}$ Hz) the detailed description of the method of measurements of the real part of the dielectric permittivity by means of a partly filled rectangle waveguide is given. We have measured the dielectric constant equal to 1.53 at a frequency $4,5 \cdot 10^{10}$ Hz. The obtained result of $\acute{\varepsilon}=1.53$ complements the result obtained previously in the range up to 10^6 Hz. On the basis of these measurements are an approximation of the frequency dependence of the dielectric constant in the range of 10^2-10^6 Hz.

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