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Frequency and Si concentration dependence of dielectric spectrum of natural zeolite composites prepared by using zeolite and silicon powders

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We present the real and imaginary part of the dielectric permittivity of natural zeolite composites prepared by using zeolite and silicon powders. The dielectric response (DR) dependences on the frequency of electric field and different Si concentrations (10-50%) are non-monotonic and a peak is observed. This peak position is practically independent on the frequency and the maximum is observed in zeolite composites which included 10% of Si-powder. Also the peak decreases by about an order of magnitude when frequency increases from 500 Hz to 5 kHz. Addition of conductive Si-particles to zeolite-powder leads to two opposite effects. Firstly, the movement of electrons in the Si-particles provides an increase of DR. Secondly, cations leaving zeolite pores can be neutralized by the particles of Si in the intercrystalline-space. Such a peculiar mechanism of recombination of Si electrons and cations from pores leads to a reduction of DR for large silicon concentrations. The contribution of free carriers in the decreasing of the DR as the frequency increases is consistent with the suggestion that the maximum peak decreases with increasing frequency.

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1. Introduction

Natural-zeolite (NZ) minerals are good sorbents and exhibit the ability to ion exchange due to their strictly defined pore size and internal cavities (≈ 4 Å). Zeolite represents microporous "sponge" with a pore volume of up to 50% of the skeleton. In Azerbaijan, it is found that 14 types of minerals of the zeolite family associate with magmatism. More than 40 types of NZs mineral are known. Geological feature of zeolite areas gives reason to believe that the territory of Azerbaijan is one of the most promising regions for NZs [1], which are found wide application in many areas.

On the basis of the radiographic and chemical analysis on alumosilicate-zeolite, it is established that the NZ examined by us is affiliated to zeolites of clinoptilolite (Cl) species [2]. The crystal structure of Cl has a monoclinic cell with the cell dimensions a = 17.74 Å, b = 17.9 Å, c = 7.4 Å, with the symmetry space group C2/m, $\beta = 117^{o}$. Crystalline structure is composed of an alternating negatevely charged alumosilicate tetrahedra AlO_4 and SiO_4, which are interconnected by nodes with a pore-nanochannels of two types A and B that dimensions 0.6 × 0.4 nm - (A type) and 0.4 × 0.4 nm - (B type) [3]. These channels are filled with the extra-framework cations that is, Na^+, K^+, Mg^{2+}, Ca^{2+}, which compensate the negative charges of the framework and a large number of molecules of H_2O-water. Water plays an important role in the stability of Cl framework. Since between the oxygen atoms of the skeleton, the positively charged ions and H_2O molecules there are hydrogen bonds, it is believed that H_2O molecules lead to an increase [5-7] of the mobility of ions in the pores space. It should be noted that infrared spectra are sensitive to change in both the hydrogen and coordination bonds in the crystal. This is the reason for our interest in the measurement of the absorption of water in Cl, where the absorption spectra of NZ-Cl in a wide frequency range from 3600 cm^{-1} to 100 cm^{-1}. Identified bands are caused by the absorption of water in the pores of the zeolite. The observed broad band at a frequency of 3470 cm^{-1} is caused by vibration of water molecules. The strongest band at a frequency of 1631 cm^{-1} confirms the higher diffusion mobility.

Under various conditions a number of works are devoted to the study of dielectric spectra of zeolites. In Ref. [8] it is 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-components 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 [9]. In this study, the NZ 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 water 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. [10] it is established that the modification of some ions increase the dielectric permittivity with respect to the original sample while others reduces. In Ref. [11], the dielectric spectra of natural Cl were measured in vacuum (0.1 Torr) and in air (at atmospheric pressure). Measurements were performed 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.

The study of the electrical properties was conducted mainly in an alternating electric field. This is due to the fact that the conductivity of zeolites is associated with the movement of ions in the zeolite pores. Previous works were devoted to ionic conductivity of zeolites was assumed that the hydration leads to a weakening of the electrostatic interaction of cations with the framework and, correspond-dingly, to decrease the barriers to their migration. The ability of the cations to diffuse through the large open zeolite structure gives the possibility of obtaining high ionic conductivity in zeolites. In recent years, there have been many attempts to investigate the possibility of management by ion transport in the external electric field. They are considered in the Ref. [12]. Electrical conductivity of zeolites at an alternating voltage is caused by the movement of positive metal ions in porous framework, and it essentially depends on the content of water in the pores. This explanation is quite suitable for alternating currents. There are not enough studies on the electrical conductivity of zeolites in a constant voltage mode. In Refs. [13-15] the zeolite plate which has been cut from a monoblock natural Cl, on micromonocrystal synthesized zeolites and on the pellets compressed from powder of NZ, respectively. At research of currents at a constant voltage the steady-state current that is not specific for ionic conductivity of the zeolites or continuously decreasing current with time are observed. Therefore controversial question is about possibility the ionic conductivity of zeolites at dc current.

Recently, there is a considerable interest to studying electric properties of zeolitic powders, films and film composites in a constant electric field. The electrical conductivity of the zeolite film exhibits ideally two modes: firstly, at low voltages, when the film acts as an insulator and the secondly after the breakdown voltage when the conductivity increases dramatically. Investigation of composite materials based on the zeolite powder is limited by problems of implementing components of a composite into the pores of the zeolite [20]. One of the attractive components for creating composite with zeolite powder is silicon particles coated with natural silicon dioxide SiO_2. The silicon dioxide which is formed on the surface of silicon is an effective absorber of water vapors [20,21]. In [22] authors studied the electrical properties of the mixture of zeolite and Si powders. The peculiarity of such composite is that both zeolite and particles of Si powder (covered by dioxide of Si) are effective absorbers of water vapors and zeolite particles do not possess electronic conductivity as opposed to particles of low-ohmic Si. It turned out that a small (10%) supplement of the Si particles to the Cl-powder leads to a substantial change in the electrical conductivity of the zeolite powder. Instead of the continuously decreesing current with time, which is typical for ionic conductivity, the steady-state current is observed at constant voltage. At the same time, at a certain feeding voltage (which depends on the air pressure) the current starts to rise sharply with increasing voltage. Considering availability of such strong effect of Si on character of the steady-state current in zeolite powder and assuming possible interaction in such system between the ions, leaving zeolite pores, with Si particles at its various concentration, we decided to investigate the conductivity at alternating current in a mixture of Cl-powder and Si with different concentration.

2. Experimental

2.1. Materials

The object of the study was to use NZ which is a Cl with low moisture 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, β= 115.2°. the chemical composition confirmed by X-ray diffraction carried out by us [6] 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. NZ powder obtained by grinding in a mortar pieces, and then processing them in a planetary sample preparation milling type FRITSCH, where they were brought to the powder state with a particle sizes of 0.1 mm. For the standard manufacture of silicon powder was used the silicon wafer factory (111) and (100) which marks the EFC (resistivity ≈ 7.5 ohm.cm). After preliminary grinding silicon particles, the zeolite powder is converted into a planetary mill for investigated samples of two types: NZ powder and the powder mixture of NZs which has silica of the following composition Si-10%, 20%, 30%, 40%, 50%.

2.2. Measurement method

For the measurement, the samples were placed in a cell between two planar electrodes, one of which is a semitransparent conductive 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 0.5 mm and a powder or plate with diameter of 1 cm. The cell connected to the LRC (impedance, resistance and capacitance) impedance meter E7-22, (frequency range 100 Hz - 1 MHz).

3. Results

Fig. 1 shows the frequency dependence of the real (ε') and imaginary (ε'') parts of the permittivity. Fig. 2 shows the frequency dependence of ε' and ε'' on the Si concen-tration. From these graphs it should be noted that:

- With increasing the frequency both for pure zeolite and for mixtures of zeolite with silicon powder frequency dependences ε' and ε'' correspond to model with one relaxation time. Differences of the curves in Fig. 1 for various concentrations of silicon are associated with differences in the parameters of the model with one relaxation time;
- In the dependence of the dielectric response on Si concentration the maximum is observed at concentration about 10% Si;
- The peak position is almost independent from the frequency;
- The maximum is reduced by about an order of magnitude for the dielectric permittivity with increasing frequency from 500 Hz to 5000 Hz;
- Change in the concentration of Si by tens of percent leads to a change in the dielectric permittivity hundreds of percent. For example at 500 Hz when the concentrations change from 10 to 30 percent, ε' varies from 570 to 130;
- At high Si concentrations a peculiar saturation takes place: at all frequencies responses approach.

Starting an explanation, it should be noted that the basic property of zeolites is the ability of ion-exchange. We believe that this property of the zeolite precisely determines the number of peculiarities of dielectric response. The fact is that during a state of thermal equilibrium in a zeolite powder the exchange of positive ions between various crystallites takes place. During the usual ion-exchange process in the pores of zeolite the substitution occurs between the same types of ions. At conditions of thermal equilibrium in the zeolite powder the same exchange process occurs, but between identical ions. In the absence of an external electric field this does not lead to new phenomena. In an external electric field at measurement of electrical conductivity, the same exchange of identical ions between different crystallites provides a continuous ionic current. For an explanation of non-monotonic dependence of dielectric response on the Si powder concentration, we shall consider from this point of view an investigated mixture of zeolite with silicon powder. Addition of the conductive Si particles to zeolite powder leads to two opposite effects. On the one hand, movement of electrons in the Si particles in the zeolite is additional in relation to mechanism of dielectric response time: Conductivity of silicon particles in the presence of an external electric field provides a contribution to the imaginary part of the dielectric permittivity and the dipole moments of localized Si particles are summarized and give the contribution to the real part of the dielectric permittivity. This leads to an increase in the dielectric response. On the other hand, positive ions from zeolite pores moving in the intercrystalline space can be neutralized by Si particles [23].

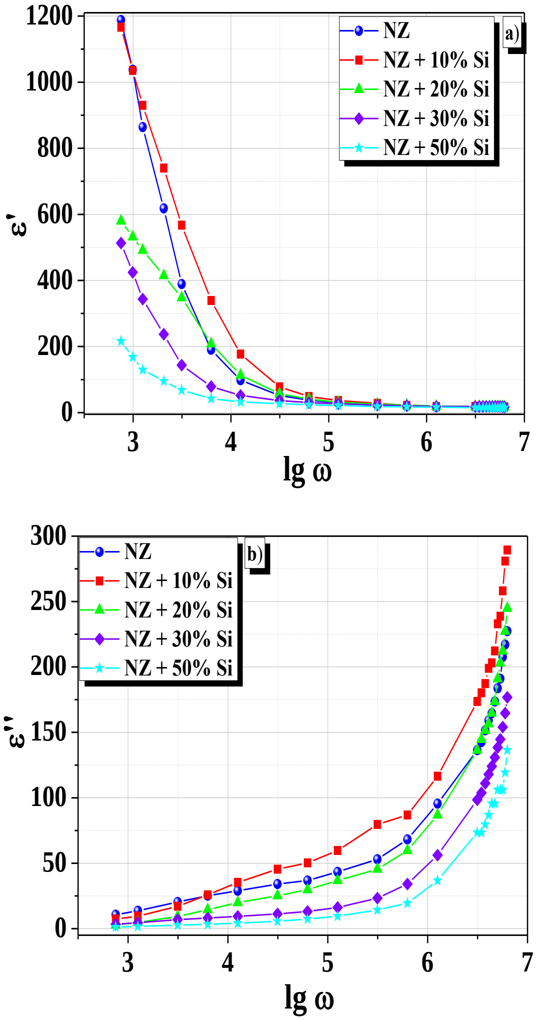

Fig. 1. Frequency dependences of the real (a) and imaginary (b) parts of the permittivity of the zeolite and mixture of the zeolite with different Si concentrations (10%, 20%, 30%, 50 %)

Such a unique mechanism for recombination of Si electrons and positive ions from the zeolite pores explains the dependence of the dielectric response time on the concentration of silicon powder that observed in our experiment. Indeed, gradually increasing from low Si concentrations leads to an increase in dielectric response time, because Si powder also contributes to the dielectric response of the zeolite powder. At the same time the recombination of Si electrons and ions in zeolite is insignificant. Moreover, decrease of the dielectric response at high Si concentrations occurs due recombination of Si electrons and zeolite ions. Recombination will continue as long as the electric field of positive charged silica particle does not stop this process. Such a mechanism is consistent with a disproportionately large change in dielectric response time at a small change in concentration of silicon powder. The strong interaction between the components of the mixture explains the nonlinear dependence of the effect of Si impurity on the experimental results of dielectric response. Such a unique mechanism for recombination of Si electrons and positive ions from the zeolite pores explains the dependence of the dielectric response time on the concentration of silicon powder that observed in our experiment. Indeed, gradually increasing from low Si concentrations leads to an increase in dielectric response time, because Si powder also contributes to the dielectric response of the zeolite powder. At the same time the recombination of Si electrons and ions in zeolite is insignificant. Moreover, decrease of the dielectric response at high Si concentrations occurs due recombination of Si electrons and zeolite ions. Recombination will continue as long as the electric field of positive charged silica particle does not stop this process. Such a mechanism is consistent with a disproportionately large change in dielectric response time at a little change in concentration of silicon powder. The strong interaction between the components of the mixture explains the nonlinear dependence of the effect of Si impurity on the experimenttal results of dielectric response.

During recombination process of positive ions with electrons of silicon particles decreasing of the energy – NΔ occurs where, Δ – is a reduction of energy as a result of recombination of one ion, N – is the number of recombined ions. At the same time, there is an increase of electric field energy of Si particles $\int \frac{\varepsilon_0 \mathrm{E}^2}{2} dV$ which are charged positively as a result of recombination. The total energy W(N) as a function of the number of recombined particles N is equal to the sum and has the following form:

$$W(N) = -N\Delta + \int \frac{\varepsilon_0 \mathrm{E}^2}{2} dV \qquad (1)$$

Silicon particle we consider as a ball with sphere D. Accordingly for electric field we use the formula of the electric field of a charged sphere;

$$E = \frac{keN}{D^2}$$

(k = 9×10^9, e = 1,6×10^{-19} – for electron).
We determine the minimum value of the function (1) equating its derivative to zero;

$$\frac{dW(N)}{dN} = 0 \qquad (2)$$

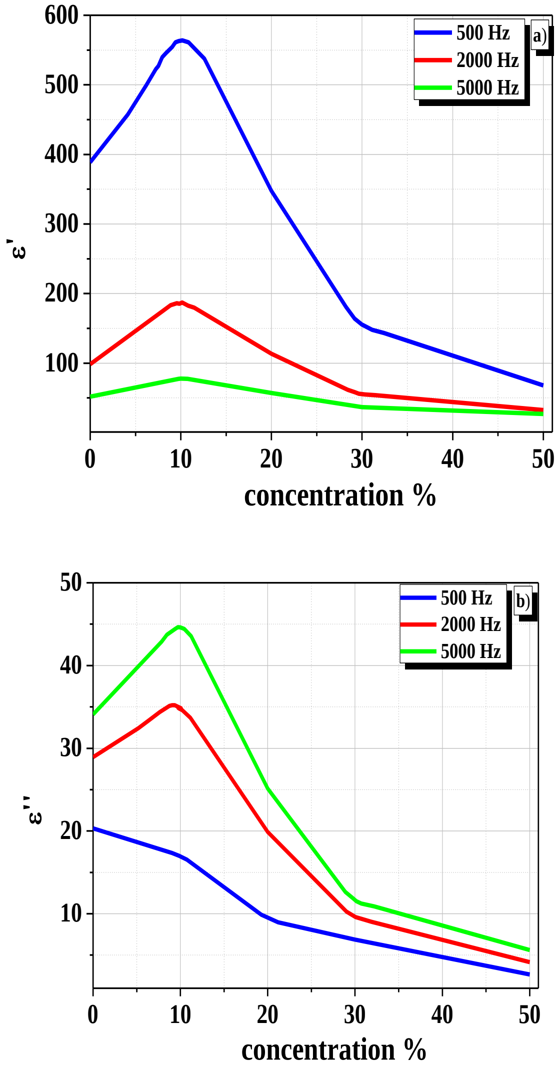

Fig. 2. Si concentration dependence of the real (a) and imaginary (b) parts of the dielectric permittivity for zeolite powder at different frequencies (500 Hz, 2000 Hz, 5000 Hz)

As a result, we obtain

$$N = \frac{D\Delta}{2\pi\varepsilon_0 k^2 e^2} \approx 10^9 D\Delta \qquad (3)$$

where D is expressed in meters and Δ is expressed in electron volts.

For an example we consider that Δ is in the order of a few eV, and D ~ 10^{-5}, and as a result we obtain: N ~ 5×10^5. Such assessment indicates that a single Si particle may recombine macroscopically large number of positive ions from the zeolite pores. This does not explain the proportionally great influence of silicon powder on the dielectric response of the zeolite mixture with silicon. In other words, the influence of the Si powder is not proportional to the volume which it occupies, because such a mechanism is determined by the contribution of impurities, not only a direct input to the response of the silicon particle, and the amount of electrons therein, recombine with the ions. It is also consistent with the fact that the position of the maximum practically independent of frequency, as in the proposed mechanism is not involved the value, neither the frequency of the applied fields. As the frequency increases the contribution of free carriers to the dielectric response decreases, the proposed explanation is consistent with the fact that with increasing frequency the maximum decreases.

A simple model with a single relaxation time is not completely describes the frequency dependence of the dielectric constants, it is explained as follows. The complexity and relationship of the electrical characteristics of such complex objects are not simply from formal transformation Maxwell's equations for the total current, and are caused by physical peculiarities of the flow in them of processes of conductivity and polarization. A simple model with a single relaxation time is not completely describes the frequency dependence of the dielectric constants, it is explained as follows.

The complexity and relationship of the electrical characteristics of such complex objects are not derived simply from formal transformation Maxwell's equations for the total current, and are caused by physical peculiarities of the flow in them of processes of conductivity and polarization. It should be noted that the classical consideration of the conduction current and displacement current, which are acceptable for an ideal conductor and an ideal dielectric is not applicable to ionically conductive NZ with developed pores system. In such complex heterogeneous media the conduction current as directed translational motion of charge carriers and the displacement current as the oscillatory displacement of bound charges should have additional phase shifts with respect to the strength *E* of external ac field, because in a porous material there is not any ideal free and ideal bound charge carriers. It is possible can be called these carriers (i.e. ions, groups and complexes) as semi-free depending on energy structure of the pore space. In the various areas of such material (e.g. at mesoscopic scale) the energy spectrum of charged particles is different. Because of this inhomogeneity, the additional phase shifts of the conduction current and displacement current should be different for various frequencies of the external field. It follows that a static and high-frequency dielectric permeability, as well as electrical characteristics of heterogeneous media, should not be a constants but complex functions of the frequency.

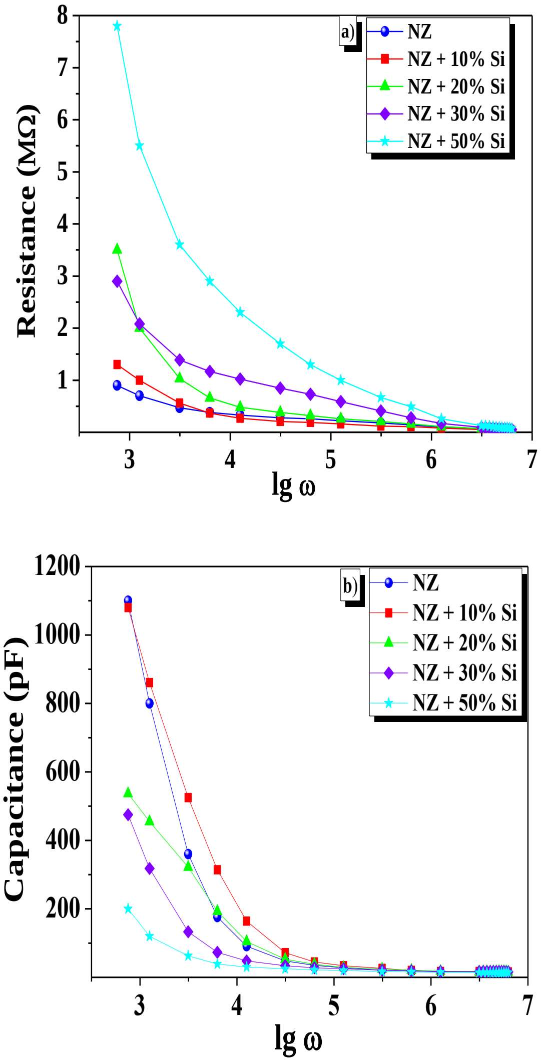

Fig. 3. Frequency dependences of the resistance (a) and capacitance (b) of the zeolite and mixture of the zeolite with different Si concentrations (10%, 20%, 30%, 50 %)

Since in our system there is a well-conducting component (i.e. silica particles), the question naturally arises related to the role of volume conduction in our investigations. In order to evaluate the role of volume conduction we have decided to give the discussions for frequency dependence of the resistance:

$$R = \frac{l}{s}\frac{1}{\sigma_0 + \frac{\omega^2\tau\left(\varepsilon_0 - \varepsilon_\infty\right)}{1+\left(\omega\tau\right)^2}} \tag{4}$$

It is shown from this formula that the resistance is constant at low frequencies. From the figures for the resistance it can be seen that at low frequencies, there are strong changes, even if the formula does not account for them. Therefore we do not consider the volume conductivity. From the graphs of the frequency dependence ε'', is impossible to see, since at low frequencies graphics merge at zero.

4. Conclusions

The dielectric response of the zeolite powder mixture with silicon powder has been investigated. The frequency dependences of the real and imaginary parts of the permittivity in the alternating field for different concentrations of silicon was measured as well as the concentration dependence of the response at different frequencies. The maximum dielectric permittivities were measured depending on the concentration silicon powder at different frequencies. It was found that a stable decrease of the dielectric response with increasing concentrations of silicon if the concentration of silicon powder is more than 10%. The explanation of the observed phenomenon is based on the assumption that the presence of two competing mechanisms which is influences on the dielectric response. Extra contribution to the dielectric permittivity which is derived from particles of Si occurs at small concentration of Si powder. At higher concentrations of silicon, recombination of the positive ions from the zeolite pores and electrons from the silicon particles lead to a reduction of the dielectric permittivities. This mechanism is based on the role of ion exchange between different zeolite crystallites.

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