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# Dielectric Properties of Natural Syrian and Armenian Zeolites

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Using an experimental arrangement, designed and manufactured locally, the electric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  and alternative current (a.c.) conductivity  $\sigma_{ac}$  of natural Syrian and Armenian zeolites were investigated in order to understand the mechanism of the electrical properties in these materials. The frequency dependence of angle tangents ( $\tan \delta = \varepsilon''/\varepsilon'$ ) of dielectric losses was also studied for both zeolites. The mentioned measuring arrangement has a configuration of an electrical bridge. The data has showed that the dielectric constant  $\varepsilon'$  and dielectric loss  $\varepsilon''$  for all studied samples decrease when increasing the frequency of the applied electrical field from 200 Hz to 1 MHz. Moreover, it was found out for all studied samples that the *ac* conductivity  $\sigma_{ac}$  increases with the frequency of the applied electrical field. The ratio of such increasing depends itself on the applied frequency.

KEY WORDS AND PHRASES: Natural zeolite, Dielectric properties, Electrical conductivity.

## Introduction

Zeolites are natural minerals that are mined in many parts of the world or synthesized by man. They are characterized by a microporous, crystalline structure consisting of a three-dimensional framework of  $\text{SiO}_4$  tetrahedra where all four-corner oxygen ions of each tetrahedra are shared with adjacent tetrahedra. Some of the quadrivalent silicon is replaced by trivalent aluminum, giving rise to a deficiency in positive charge. This charge deficiency is balanced by the presence of mono and divalent cations located in the pores. These cations are highly mobile and can be exchanged for other cationic species. The Si/Al ratio of natural zeolite is in the range of 1–6. Loosely bound water is also present in the pores of natural zeolites and range from 10–20 wt. % of the dehydrated phase. Zeolites have a void spaces (cavities or channels) that can host cations, water or other molecules. Cavities in zeolites enable them to screen molecules and sieve cations. Cation exchange capacity is primarily a function of the degree of Al substitution for Si in the structure: the greater the substitution, the higher is the deficiency of the positive charge and the greater is the number of alkali cations needed to achieve electrical neutrality. However, cation exchange capacity also depends on other factors, such the exposure of the zeolite to cations that are easily trapped in the structure but which can not be removed easily. The size of the cations also has an effect on cation exchange capacity. The large cavities and entry channel of zeolites are generally filled with water molecules that form hydration spheres around the exchangeable cations.

The physical and chemical properties of natural zeolites in the fact that they can capture and immobilize ammonium ions, water, and certain cations has resulted in numerous investigations into developing agricultural and/or horticultural applications for them. The following uses of zeolites have been extensively investigated: holding

and slow releasing valuable nutrients to plants, mainly ammonium; uses in conjunction with nitrogen ( $\text{NH}_4^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}_2^+$ ), calcium ( $\text{Ca}_2^+$ ) and trace elements; promoting better plant growth by improving the value of fertilizer; prevention of plant burning from over-use of fertilizers by trapping and slowly releasing valuable nutrients; improving the cation exchange capacity of soil resulting in less fertilizer requirements; and improving the water retention of soil. However, U.S. Pat. No. 5,900,387 reports experiments on clinoptilolite which has been reported as having a high affinity and selectivity for ( $\text{NH}_4^+$ ). Moreover, nowadays an extensive attention is paid on Jordanite. The zeolitic component of Jordanite is primarily phillipsite, but a minor amount of chabazite may also be present. In this embodiment, the phillipsite may be present in amounts ranging from about 10 to about 90 wt. % and the chabazite in amounts ranging from about 1 to about 20 wt. %.

The investigation of dielectric properties of zeolite during the process of hydration and dehydration gives an important information about its sorption capacity and catalytic activity [1–7]. The measurement of electric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  and a.c. conductivity  $\sigma_{ac}$  of zeolites, having ionic or mixed ionic/electronic conductivity, is used generally to investigate the zeolite sorption properties of water vapor, since the absorbed water molecules in zeolites play a basic role in electrical behaviors [8] of these materials at room temperature. The aim of this work is to shed a light on this question regarding Syrian and Armenian natural zeolites which contain clinoptilolite (the Armenian one) and the main components of Jordanite (the Syrian ones).

1. Experimental Arrangement

In this work, the investigated samples have been prepared from grounded Syrian (S) and Armenian (A) natural zeolites. The Armenian zeolite, denoted by A12, contains up to 85 % of clinoptilolite with a ratio of Si/Al equal to 9 and amorphous  $\text{SiO}_2$  less than 3 %. The Syrian zeolitic tuff contains mainly about 50 % of three types of zeolite (analcime, phillipsite and chabazite). The chemical composition of the studied samples is given in the Table 1. The samples were ground and pressed at  $1470 \text{ N/cm}^2$  into pellets of 2–3 mm of thickness. From these pellets, samples of  $30 \text{ mm}^2$  in surface were taken mechanically. Both plate surfaces of each sample were coated using silver contacts and thermally treated at temperature  $120^\circ\text{C}$  for two hours followed by thermal treatment at  $220^\circ\text{C}$  for two extra hours. This treatment was performed in order to obtain reliable good silver contacts.

The chemical composition of the studied samples

Table 1

| L.I.  | P <sub>2</sub> O <sub>5</sub> | Cr <sub>2</sub> O <sub>3</sub> | Mn <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | MgO   | Fe <sub>2</sub> O <sub>3</sub> | CaO   | K <sub>2</sub> O | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Sample |
|-------|-------------------------------|--------------------------------|--------------------------------|------------------|-------|--------------------------------|-------|------------------|-------------------|--------------------------------|------------------|--------|
| 14.19 | —                             | —                              | —                              | 0.20             | 1.28  | 2.23                           | 4.9   | 2.22             | 0.79              | 11.69                          | 67.11            | A12    |
| 12.3  | 0.44                          | 0.03                           | 0.2                            | 1.60             | 12.21 | 11.68                          | 8.77  | 1.01             | 1.22              | 10.48                          | 39.51            | 2S14   |
| 14.10 | 0.46                          | 0.03                           | 0.17                           | 1.48             | 11.09 | 10.41                          | 11.01 | 0.89             | 0.93              | 9.98                           | 38.69            | 4S14   |
| 15.16 | 0.52                          | 0.03                           | 0.17                           | 1.60             | 9.74  | 10.65                          | 11.92 | 1.08             | 0.99              | 10.15                          | 37.64            | 6S14   |
| 16.52 | 0.52                          | 0.03                           | 0.15                           | 1.37             | 8.55  | 8.97                           | 14.95 | 0.84             | 0.75              | 9.80                           | 37.14            | 8S14   |
| 10.98 | 0.41                          | 0.04                           | 0.22                           | 1.64             | 14.17 | 13.20                          | 6.73  | 1.02             | 1.13              | 10.42                          | 39.95            | 10S14  |
| 10.46 | 0.49                          | 0.03                           | 0.20                           | 1.84             | 9.99  | 12.02                          | 8.24  | 1.13             | 1.50              | 11.65                          | 40.76            | 12S14  |
| 10.71 | 0.47                          | 0.03                           | 0.18                           | 1.75             | 10.65 | 11.75                          | 8.95  | 1.13             | 1.66              | 10.97                          | 40.17            | M5     |
| 9.28  | 0.52                          | 0.03                           | 0.20                           | 2.10             | 9.01  | 12.60                          | 8.26  | 1.24             | 1.45              | 13.04                          | 41.36            | 16S14  |
| 9.31  | 0.49                          | 0.03                           | 0.19                           | 1.92             | 10.45 | 11.99                          | 8.18  | 1.19             | 1.43              | 12.00                          | 41.08            | 18S14  |
| 9.24  | 0.47                          | 0.03                           | 0.19                           | 1.87             | 10.62 | 12.30                          | 7.96  | 1.18             | 1.65              | 11.63                          | 41.23            | 20s14  |

The measurement of electric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  of the studied samples was carried out by using a special and nonstandard arrangement designed and manufactured locally. The mentioned arrangement allows to measure electric permittivity corresponding to electrical field with frequencies varying from 200 Hz to 1 MHz and with sinusoid applied voltage amplitude of 25 mV at the contacts of the sample. This measuring arrangement has a configuration of an electrical bridge. In addition to the alternative electric field a direct current (*dc*) electric field could be applied at the studied sample. The *dc* voltage could vary from 0 to  $\pm 20$  V. The scheme of the arrangement is shown in Figure 1. The unbalance signal of the bridge is applied, after magnification, to the inputs of lock-in detectors while the conductivity and capacitance of the samples are measured at the output of these detectors. The capacitance was measured using the reading of calibrating condenser ( $C_c$ ) at the zero-th indication of lock-in detector regarding  $C$ . In this arrangement three measuring transformers were used over the frequency interval ranging from 200 Hz to 1 MHz.

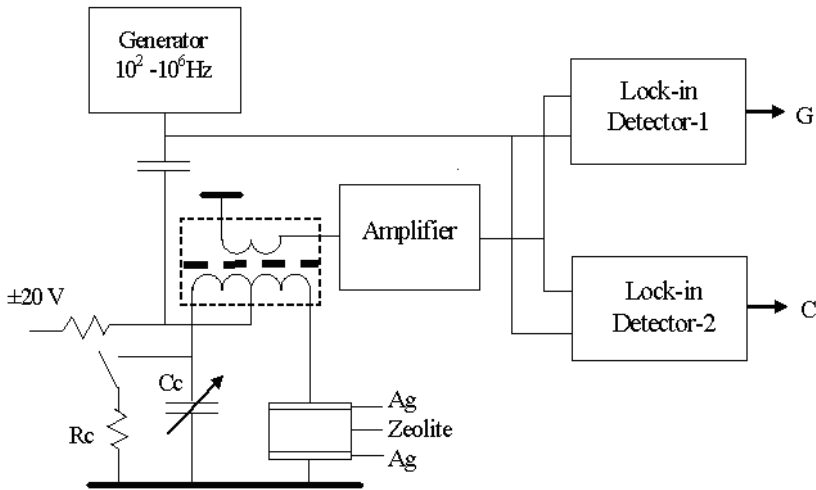


Figure 1. Scheme of the measuring arrangement:  $R_c$  stands for calibrating resistor,  $C_c$  stands for calibrating condenser

The accuracy of the measurement of the dielectric parameters is about 7%. Here it should be noted that the measurement of dielectric parameters of the studied samples was carried out in the air at room temperature. The relative humidity of the ambience during the experiments was varied from 50% to 60%.

## 2. Experimental Results and Discussion

The electric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  and a.c. conductivity  $\sigma_{ac}$  of zeolite give an important information to understand the mechanism involved in the electrical conductivity in these materials. Figures 2 and 3 show the frequency dependence of dielectric constant  $\varepsilon'$  and dielectric loss  $\varepsilon''$  of the studied samples respectively. It is seen from these figures that the behavior of these two parameters is qualitatively similar regarding their dependence on the frequency of the measured electrical field. The obtained data show that the dielectric constant  $\varepsilon'$  and the dielectric loss  $\varepsilon''$  of all studied samples decrease when we increase the frequency of the applied electrical field from 200 Hz to 1 MHz. This property is characteristic for both natural and synthetic zeolites US-HY type [7]. Another characteristic property is that the dielectric parameters have relatively high values and may change in a large interval of frequency.

Moreover, the dielectric response of zeolites is highly sensitive to the water content of samples. It is supposed that electrical dipoles, which appear in the sample as a

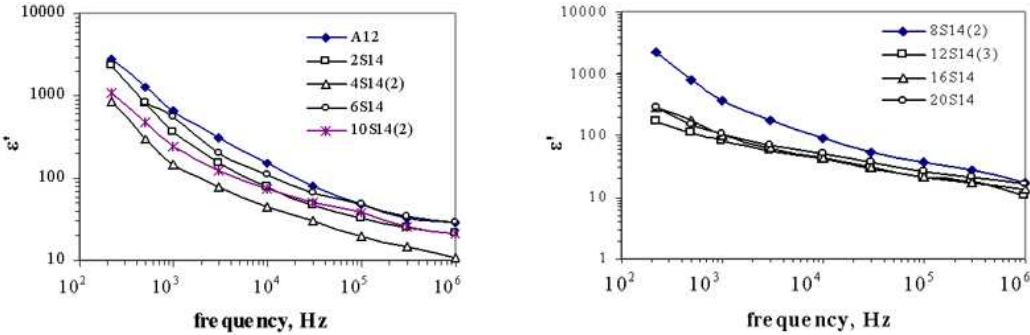


Figure 2. The frequency dependence of dielectric constant  $\epsilon'$  of the studied samples

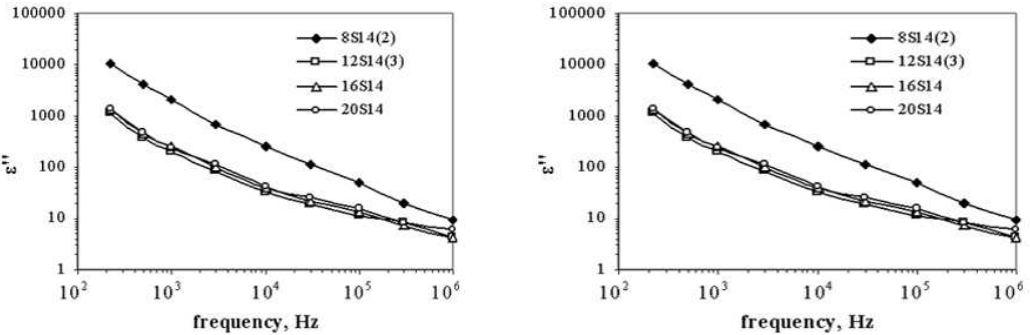


Figure 3. The frequency dependence of dielectric loss  $\epsilon''$  of the studied samples

result of formation of  $H^+$  and  $OH^-$  forms of adsorbed water in the crystalline cells, are mainly responsible for the dielectric response. In order to somehow verify this assumption, the clinoptilolite sample was thermally treated at temperature of  $8000^{\circ}C$  for 100 min. As a result of this treatment the crystalline structure of the studied sample disappeared totally according to X-ray diffractometric (XRD) investigation (not shown in this paper). When we measured the dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  of the studied sample before and after the thermal treatment we found out that the values of these two parameters largely decreased after treatment. The water content in the studied sample after treatment was equal to half its value before treatment. This experimental fact could be taken as an indication of the validity of the given assumption.

The frequency dependence of angle tangents ( $\tan \delta = \epsilon''/\epsilon'$ ) of dielectric losses is given in Figure 4. The angle tangents curves show some special features for all studied samples. The  $\tan \delta = \epsilon''/\epsilon'$  decreases when increasing the frequency of the applied electrical field. At frequencies near to 1 MHz, the values of  $\tan \delta = \epsilon''/\epsilon'$  for all the studied samples are very close to each other. The second feature is that  $\tan \delta = \epsilon''/\epsilon'$  for all studied samples differs significantly from one sample to another in both its value and the character of the low frequency dependence of the applied electrical field. Some of these figures have a wide maximum while others tend to show this wide maximum. The appearance of wide maximum of  $\tan \delta = \epsilon''/\epsilon'$  at low frequency of the applied electrical field is an indication to the fact that the studied zeolitic samples are polar materials. Indeed, the molecules of these materials contain groups having constant dipole moment [9]. In such materials a relaxation polarization and losses are developed. When the frequency of the applied field increases the values of  $\epsilon'$  decrease while the values of  $\epsilon''$  pass through a maximum. However, as it is seen from Figure [2], the maximum of  $\epsilon''$  is not observed. This is probably due to the

relatively high value of the initial frequency of the applied field. Thus, it is probable to observe this maximum at frequency lower than 200 Hz.

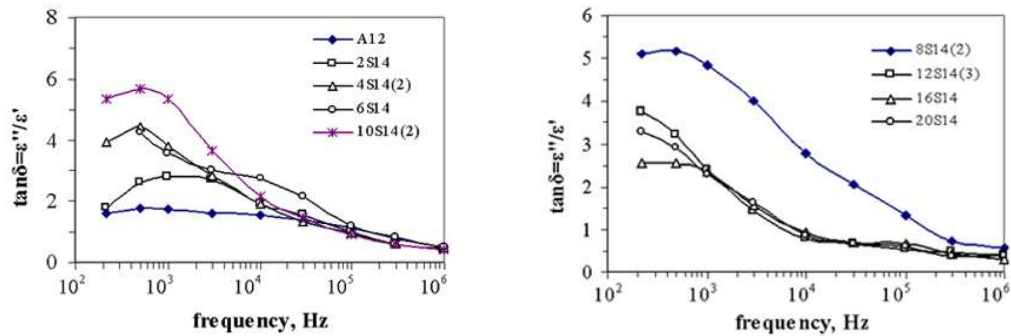


Figure 4. Frequency dependence of angle tangents of dielectric losses of studied zeolitic samples

Here it should be noted that  $\tan \delta$  is a parameter which does not depend on the density of electrical dipole moments of the studied materials but it characterizes these dipoles. In fact,  $\tan \delta$  constitutes a source of information for the structural changes in these dipoles and their ambience surrounding. From this point of view, the significantly observed differences of  $\tan \delta$  parameter (see Fig. 4) allow us to assume that the structure of the crystalline cells of the studied samples is quite different. Moreover, this can be due, in particular, to the availability of different defects and impurities in the crystalline cells.

The frequency dependence of alternative current (*ac*) conductivity  $\sigma_{ac}$  is shown on Figure 5. The *ac* conductivity  $\sigma_{ac}$  could be calculated by using the well-known formula  $\sigma_{ac} = \varepsilon_0 \omega \varepsilon'' = 2\pi f \varepsilon_0 \varepsilon''$ , where  $\varepsilon_0$  is the vacuum permittivity,  $\omega$  — the angular frequency [7]. For all the studied samples it was found that *ac* conductivity  $\sigma_{ac}$  gets larger when the frequency of the applied electrical field increases. The ratio of the increments depends itself on the applied frequency. At very low frequencies there is a region where *ac* conductivity  $\sigma_{ac}$  remains practically constant, while at higher frequencies a monotonous increasing of *ac* conductivity  $\sigma_{ac}$  with frequency is observed. Similar results were found for US-HY type zeolite [7] and for synthetic dehydrated zeolites NaY and HY [10,11].

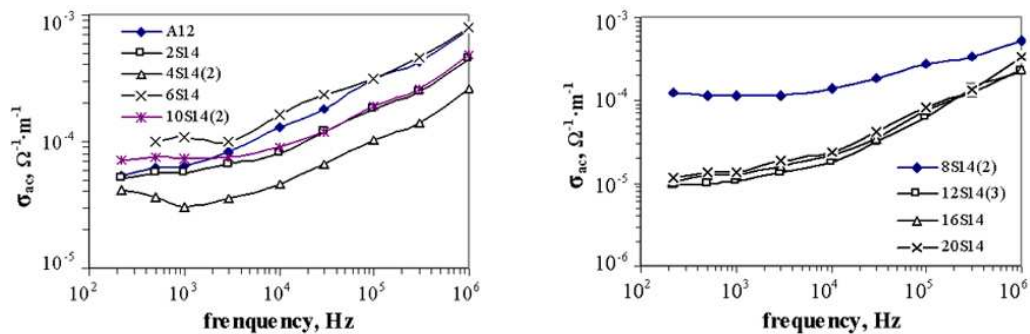


Figure 5. Frequency dependence of *ac* conductivity of the studied samples

In addition to the above mentioned experimental arrangement, a standard impedance meter was used to measure the electrical conductance and capacitance by using a special measuring cell. Samples were ground and then pressed in pellets of 2–3 mm in thickness and of 25 mm in diameter at about 1470 N/cm<sup>2</sup> of pressure. Al electrodes were vacuum deposited on both sides of the samples. The prepared

electrodes were circular in shape with diameter of about 20 mm. After that, the samples were thermally treated at temperature of 120°C for two hours followed by additional two hours of thermal treatment at 220°C. Data were collected in voltage drive mode employing a linear sweep over the frequency range 100 kHz to 13 MHz. The amplitude of the measure *ac*-voltage signal was 1 V. PC interface was used for data acquisition where connection to the frequency response analyzer was performed by screened coaxial cable of 1m in length. The obtained data agree with the mentioned results above.

## Conclusions

Finally it should be mentioned here that the main results obtained in this work are:

- The dielectric constant  $\varepsilon'$  and the dielectric loss  $\varepsilon''$  of all studied samples decrease when we increase the frequency of applied electrical field. This behavior agrees well with the results found out in other works and could be taken as a characteristic for both natural and synthetic zeolites.
- The dielectric response of zeolites is highly sensitive to the water content in the studied samples.
- $\tan \delta = \varepsilon''/\varepsilon'$  for all studied samples differs significantly from one sample to another in both its value and the character of the low frequency dependence of the applied electrical field.
- The obtained frequency dependence of alternative current (*ac*) conductivity  $\sigma_{ac}$  of the studied samples agrees well with the finding of others studies.
- $\tan \delta$  characterizes electrical dipole moments of the studied materials and constitutes a source of information for the structural changes in these dipoles and their ambience surrounding.

## References

1. *Breck D. W.* Zeolite Molecular Sieves: Structure, Chemistry and Use. — New York: Wiley, 1974.
2. *Feodorov V. M., Glazun B. A.* // USSR AS News, Chem. — 1964. — P. 1930.
3. *V. M. Feodorov, B. A. Glazun, I. V. Gilenkov, M. M. Dubinin* // USSR AS News, Chem. — No 7. — 1966. — P. 1129.
4. *A. Delgado, A. R. Ruiz-Salvador, G. Rodrigez-Fuentes, A. Berazain* // Proc. Conf. Ree. IEEE Inter. Symp. Elect. Insul. Soc. — Montreal, Canada: IEEE New York, 1986. — P. 866.
5. *Concepcion-Rosabal D., Balmaceda-Era J., Rodrigez-Fuentes G.* // Micropor. Mesopor. Matter. — Vol. 38. — 2000. — P. 161.
6. *Sayed M. B.* // Zeolites. — Vol. 16. — 1996. — P. 157.
7. *Sayed M. B.* // Micropor. Mesopor. Matter. — Vol. 37. — 2000. — P. 107.
8. *Simon U., Franke M. E.* // Micropor. Mesopor. Matter. — Vol. 41. — 2000. — P. 1.
9. *Borisova M. E., Koikov S. N.* The Physics of Dielectrics. — Leningrad, 1979. — (in Russian).
10. *Abdoulaye A. et al.* Some remarks on the ionic conductivity in NaY dehydrated zeolite // Ionics. — Vol. 2. — 1996. — P. 39.
11. *Abdoulaye A. et al.* Polarization conductivity in dehydrated zeolite NaY and HY // Micropor. Mesopor. Matter. — Vol. 3. — 1997. — P. 63.

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## Диэлектрические свойства натуральных цеолитов

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В работе было проведено исследование диэлектрической проницаемости  $\varepsilon = \varepsilon' - i\varepsilon''$  и проводимости по переменному току  $\sigma_{ac}$  натуральных цеолитов из Сирии и Армении с целью изучения электрических свойств этих материалов. Также была исследована зависимость тангенса угла диэлектрических потерь ( $\tan \delta = \varepsilon''/\varepsilon'$ ) от частоты для обоих видов цеолитов. Экспериментальная установка имела вид электрического моста. Полученные данные показали, что диэлектрическая постоянная  $\varepsilon'$  и диэлектрические потери  $\varepsilon''$  для всех исследованных образцов уменьшаются с увеличением частоты приложенного электрического поля от 200 Гц до 1 МГц. В то же время для всех исследованных образцов проводимость по переменному току  $\sigma_{ac}$  увеличивается с ростом частоты. Характер роста зависит от частоты приложенного поля.