REVISTA CUBANA DE FÍSICA Vol.VIII, No.1, 1988

Dielectric spectrometry of sodium and calcium clinoptilolite and mordenite

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SHORT COMUNICATION

The studies of dielectric properties of zeolites has become a useful method to understand its structure, ionic composition, catalytical properties, etc. (1-5).

In this paper we study the dielectric spectra of homoionic sodium and calcium clinoptilolite and mordenite obtained from the deposits in Camagüey, Cuba, named CC3 and MC4 whose elemental composition and phase analysis are shown in table 1.

The homoionization process was carried out by boiling the samples for eigth hours, five times with a fresh solution three molar of Na_2NO_3, and $CaNO_3$. Subsequently, they were washed carefully twenty times with distilled water in an attempt eliminate the superficial conduction.

The measurements were made using equipment composed of two principal parts: a vacuum line with a cilindrical capacitor and a dielectric sensor circuit (fig.1).

The samples in the form of a powder (0.6 to 1.6 mm of particle diameter), were put into the cilindrical capacitor (fig.2), and heated for 18 hours at 573 °K, in the vacuum (10^{-5} Pa). After this, a weak electric field was applied to the capacitor (with the sample) with a variable frecuency ranging from 0.04 to 100 Khz., then with the help of the operational amplifier (fig.1), the variations of the input and output voltages were measured, obtainning the capacity through the formula:

$$V_0 = (C_x/C_r)V_1$$

where C_r is the capacity of a reference condenser and C_x is the capacity of the sample.

In this way we obtained the variation of E(permitivity) vs. log f, considering:

$$E(f) = C_x/C_v$$

C_v is the capacity of the cilindrical condenser when it is empty.

The sensor circuit was calibrated with the help of a standard Phillips condenser with an accuracy of 0.2 pF.

The measurements were taken at three different temperatures, i.e.: 300, 373 and 473 ^{0}K. The accuracy in all measurements was better than 5 percent.

The results of our study are the first regarding homoionic zeolites, using cuban natural samples, by the dielectric spectrometry in a wide range of frecuencies.

The analysis of the results presented in figures: 3, 4 and 5, leads us conclutions regarding the structures of the zeolites.

Refering to the figures we can observe the following:

The behaviour of E is the same at both temperatures when the frecuency is increased. For the highest frecuencies, in the selected range E comes up to a constant value, which is related to the framework polarization of each zeolite. On the other hand the principal effect of the increase in temperature is the displacement of the curve to greater values of E. This happens because when we increase the temperature there appear new possibilities of polarization in the zeolite that did not occur at low temperatures. The differences between the behaviour of E for the two cations employed is due to two principal facts: the sodium has more mobility than calcium inside the zeolite (6), and the population of sodium is larger than the population of calcium in the aluminosilicates, both reasons determine that there are more stages of polarization for the sodium and therefore the polarizability in this case is increased.

On the other hand at room temperature, it can be noted that Ca in clinoptilolite is less mobile than in mordenite. The opposite occurs in the case of Na. This is related to the fact that Ca in clinoptilolite is isolated in the eigth member channel (7) and in both mordenite and clinoptilolite is situated in the main channels (8) where is disposed Ca for mordenite too.

The spectra obtained have not been reported in the case of other cuban mineral deposits.

TABLE 1

CHEMICAL COMPOSITION (%)

	CC3	MC4
SiO_2	71.3	70.0
Al_2O_3	11.8	9
Fe_2O_3	3.4	3.7
CaO	6.0	5.1
MgO	0.3	0.3
Na_2O	0.4	0.8
K_2O	2.6	2.1
H_2O	14.5	16.0

PHASE COMPOSITION (%)

	CC3	MC4
CLINOPTILOLITE	85 5	----
MORDENITE	----	85 5
OTHERS	15	15

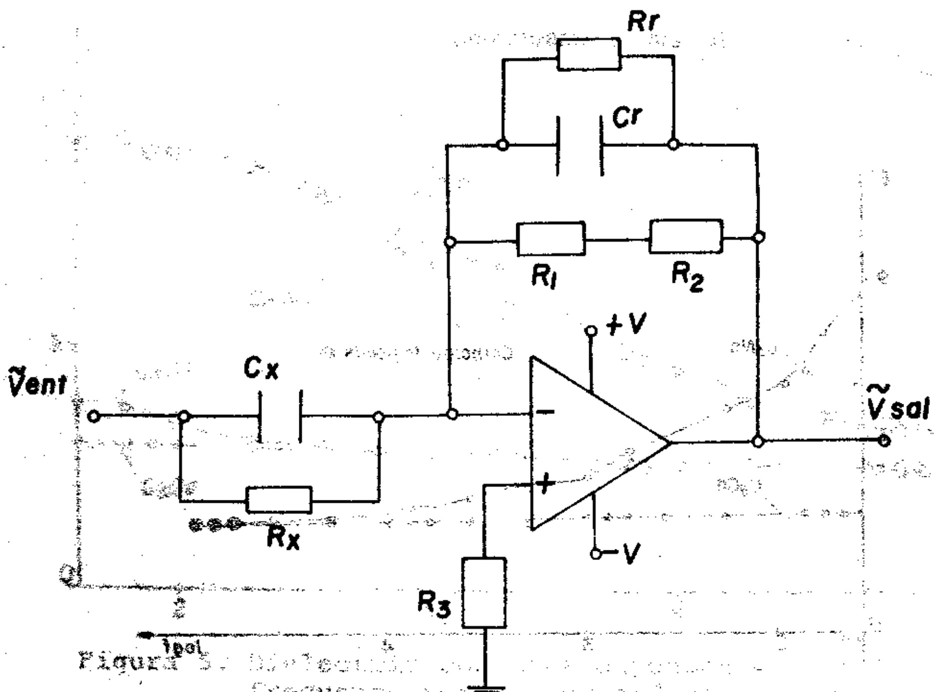

Figura I. Dielectric sensor circuit.

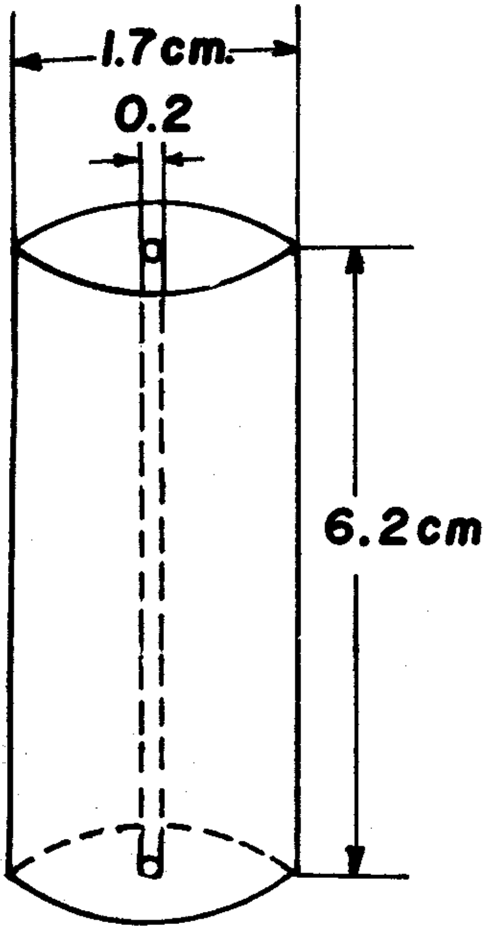

Figura 2. Cilindrical Capacitor

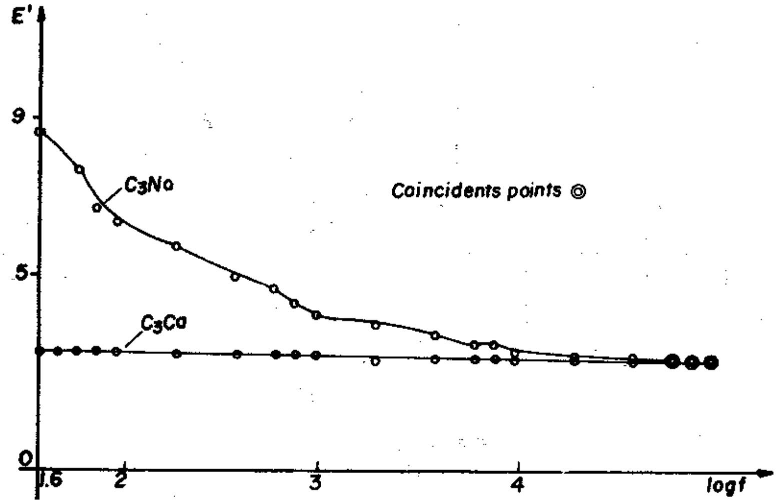

Figura 3. Dielectric constant dependence with the frecuency for sodium and calcium clinoptilolite, (C3Ca, C3Na), AT 300°K.

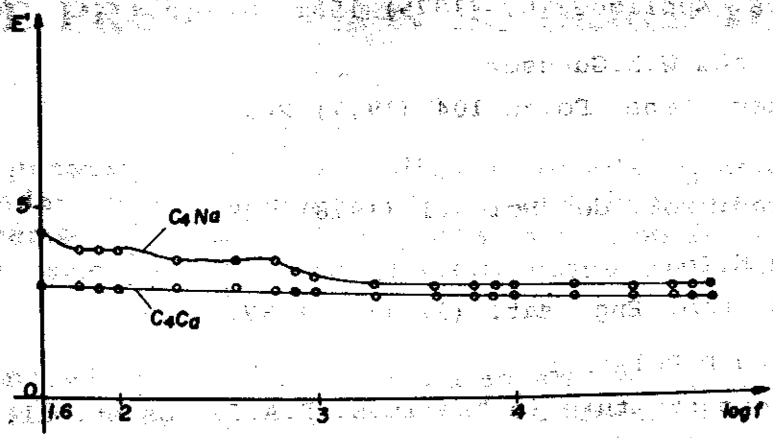

Figura 4. Dielectric constant dependence with the frecuency for sodium and calcium mordenite, (C4Na, C4Ca), AT 300°K.

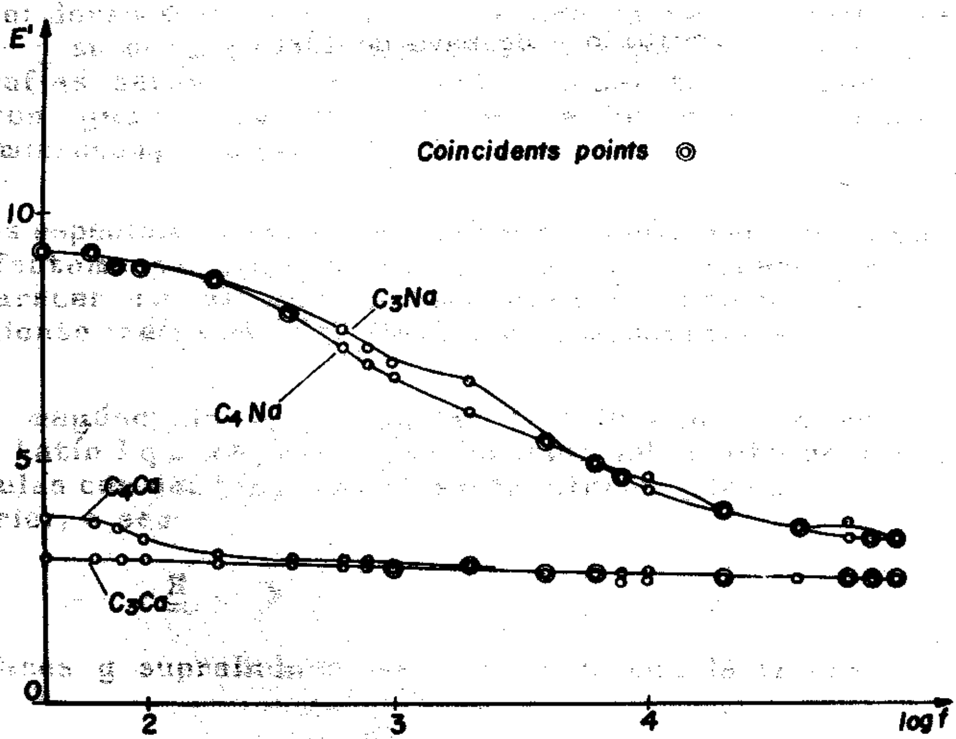

Figura 5. Dielectric constant dependence with the frecuency for sodium and calcium clinoptilolite and mordenite AT 373°K.

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Recibido 6 de mayo de 1986