

Dielectric Study of Heulandite

¹Dr. V.P.Deshpande, Prin.B.T.Bhoskar²

¹Shivaji college kannad Dist. Aurangabad Pin 431103

²Nutan mahavidyala sailu Dist.Parbhani

Abstract:- Zeolite Heulandite belongs to Group VII were collected near Ellora Ajanta belt. Characterization was made using XRD,IR at NCL Pune. Dielectric study was made using LCR Bridge.

Keywords:- Heulandite, Characterization, Dielectric study

I. HEULANDITE

Heulandite zeolites are among the most abundant useful zeolites found in the nature with Si/Al ratio ranging from 3 to 5. the general formula for Heulandite is [(Na,K) Ca₄(Al₉ Si₂₇ O₇₂) 24 H₂O]. Heulandite is determined as the mineral with a ratio Si/Al < 4.They are monoclinic zeolite minerals C2/m group with the following unit cell parameters a

a=17.73 Å°, b=17.92 Å°, c=7.43 Å°, β=116.24 ° (1)

Their structure is characterized by the large intersecting open channels of 10 and 8 member tetrahedral rings. In natural zeolites these channels are predominantly occupied by Na , K, Ca and H₂O (2). The kind and the population of channel cations influence the stability of the cavities of a zeolite and play role, of the crucial importance, in it's thermal behavior (3). The cation positions are found in the channels of a hydrated natural, “Heulandite”, group zeolites (4). The key difference between Heulandite and Clinoptilolite is thermally stable to temperature in excess of 450°C, while Heulandite undergoes structural collapse below 450°C.

It is well known that Heulandite and Clinoptilolite react differently up on heating, depending on their chemical composition (5)

II. SAMPLE PREPARATIONS

Heulandite was collected from the quarries of Ajanta – Elora caves, Marathwada. Sample crushed and sieved to get 106 μm sized crystals. For ion exchange sample is treated with 1 M solution of Ammonium Nitrate with stirring at 95°C for six hours. NH₄ ion exchanged form of Clinoptilolite is heated at 250°C for 48 hours for getting H- Heulandite.

III. CHARACTERIZATION

X-ray diffraction: For the characterization of Heulandite, X – Ray diffractograms were recorded between 2θ values from 5° to 50° on Phillips (PW 1710) having wavelength 1.54056 Å°. Different three forms of Heulandite are recorded & result of d values are reported in table 1

IR

The IR spectra of Heulandite were recorded on Perkin's Elmer 221 spectrophotometer in the frequency range 400 to 4000 cm⁻¹ of parent form, NH₄ – form, Parent at 100 °C, Parent at 150 °C, parent at 200 °C & H – form of Heulandite.

The observed IR bands and assignments are given in table 2

IV. CHEMICAL FORMULA

Chemical formula for Heulandite is as follows

a) Parent form

Na_{1.54} K_{0.95} Ca₃ [Si_{26.66} Al_{18.49} O₇₂] 29 H₂O

H – form Heulandite

H_{2.95} Na_{0.54} Ca₁ [Si_{26.66} Al_{18.49} O₇₂] 29 H₂O

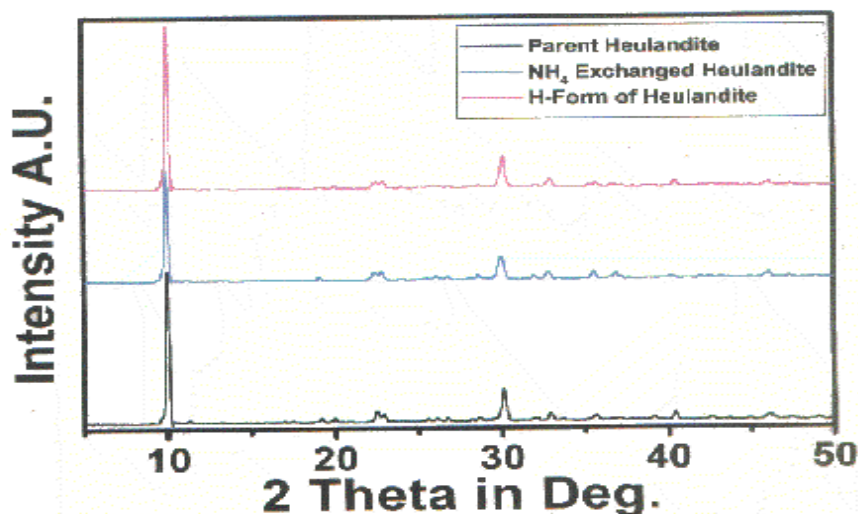


Fig. 1 XRD of Heulandite

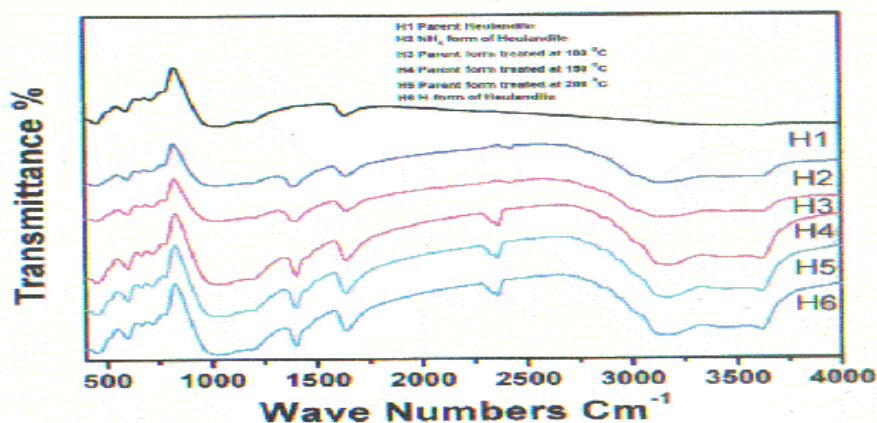


Fig. 2 IR OF Heulandite from 400-4000

V. RESULTS AND DISCUSSION

XRD:- XRD pattern of the parent Heulandite NH₄ - exchanged Heulandite and H- form Heulandite is shown in fig 1. From diffract gram we conclude the crystalline nature of Heulandite d -values are compared with standard 'd' values. This confirms the Heulandite structure. From the three diffractograms we come to the point that there is no major change in these three forms of Heulandite samples. This confirms the stability of Heulandite zeolite.

IR- From IR studies external linkage, Asymmetric stretch is observed at 1200 cm⁻¹ and symmetric stretch is at 795 cm⁻¹. In water bands region hydroxyl stretch is observed at 3740 cm⁻¹ & water bands assigned at 1655 cm⁻¹ for Internal tetrahedral (Structure sensitive) mode Asymmetric stretch is at 1095 cm⁻¹ & symmetric stretch is 750 cm⁻¹ from the IR bands of parent form, NH₄ - form & H-form of Heulandite it is observed that there is no major change in bands expect water bands. This confirms the stability of Heulandite zeolite.

Sample Name	External linkage cm ⁻¹ Str. sensitive		Double ring	Internal Tetrahedral Str Insensitive cm ⁻¹		T – 0 Bend	Water Bands	
	Asymmetric Stretch	Symmetric stretch		Asymmetric Stretch	Symmetric stretch		OH-stretch	H ₂ O Bands
Heulandite	1200	795	599	1095	750	490	3740	1655

Table 2 IR assignments in Cm⁻¹

2 Theta	d- Value	Peak Width	Intensity
9.895	8.9315	0.08	100
11.11	7.9573	0.24	2
13.12	6.7424	0.64	0.7
15.83	5.5938	0.2	1.6
16.895	5.2435	0.12	2.4
19.08	4.6476	0.16	4.5
22.2	4.001	0.28	12
22.715	3.9114	0.12	11.7
25.02	3.5561	0.12	1.3
25.92	3.4346	0.16	2.3
26.325	3.3827	0.12	3.6
26.82	3.3214	0.24	1
28.21	3.1608	0.12	3.8
30.02	2.9742	0.16	12
31.885	2.8044	0.32	2.6
32.685	2.7375	0.28	4.9
35.35	2.537	0.24	1.8
36.775	2.4419	0.64	1.8
39.775	2.2655	0.48	0.3
44.74	2.0239	0.32	0.3
45.715	1.983	0.24	1
47.11	1.9275	0.32	0.6
48.66	1.8697	0.24	0.8
49.21	1.85	0.06	0.3

Table 1 - XRD Data for Heulandite (After Background Subtraction)

IV. DIELECTRIC STUDY DIELECTRIC CONSTANT

The relative permittivity, ϵ characterizes a materials ability to store charge. This property is often referred to as the dielectric constant

$$\epsilon' = C.d / A. \epsilon_0$$

where d = thickness of the pellet

A = area of pellet

ϵ_0 = permittivity of free space

C = capacity with the dielectric

Dielectric loss:

When alternating field is applied to a capacitor containing a lossy dielectric the charging current is no longer 90° advanced from the voltage but some smaller angle 90- δ , where δ is the loss angle. For such a case it is convenient to express the relative permittivity in a complex form as

$$\epsilon^* = \epsilon' + i\epsilon''$$

Where ϵ^* is the complex relative permittivity ϵ'' is the measure of the heat related loss in the material Current in capacitor $\tan \delta = \epsilon'' / \epsilon'$

Dielectric relaxation:

It is defined as decay of polarization with time 10⁻¹² to 10⁻¹⁰ second. It occurs when electric field that induces polarization in dielectric is removed. The material takes a certain time to return to molecular disorder and polarization subsides exponentially with time constant (relaxation time)

There are two types of relaxation one is α and other is β . α relaxation occurs at low frequency due to micro brownian motion within chain

β Relaxation occurs at higher frequency due to dipole orientation as well as torsional movement of chains

Reax time $T = \epsilon'' / \omega \epsilon'$

Where $\omega = 2 \pi f$

V. CONDUCTIVITY

Compared with other ionic crystalline solids zeolites have a high electric conductivity. This conductivity results from the great mobility of the exchangeable cations. Thus zeolites can be regarded as weak electrolytes when Si /Al ratio increases there is a reduction in the number of negative charges per unit of volume and thus the distance between negative charges becomes larger. This would imply a lower probability of finding a free site at a given distance and results in a reduction in measured total conductivity

$$\text{Conductivity } \sigma = \omega \epsilon_0 \epsilon''$$

Dielectric Constant (ϵ'): Fig 5 indicates the change in dielectric constant with frequency increases ϵ' decreases up to 6000 KHz. Then from 8000 KHz ϵ' increases Increase in ϵ' is observed with increase in thickness of the samples.

Dielectric Loss ϵ'' : Fig 6 Shows the variation of ϵ'' with frequency. There is decrease in ϵ'' with increase in frequency. Decrease in ϵ'' up to 5000 KHz is slow but decrease in ϵ'' is fast at 6000 KHz. Again ϵ'' increases up to 10,000 KHz & then it decreases.

Relaxation Time (τ): Fig 7 shows the variation of Relaxation time against frequency graph shows that there is decrease in relaxation time with increase in frequency.

A.C. Conductivity (σ): Fig 8 shows the increase in a.c. conductivity with increase in frequency also σ increases with increase in thickness of the sample

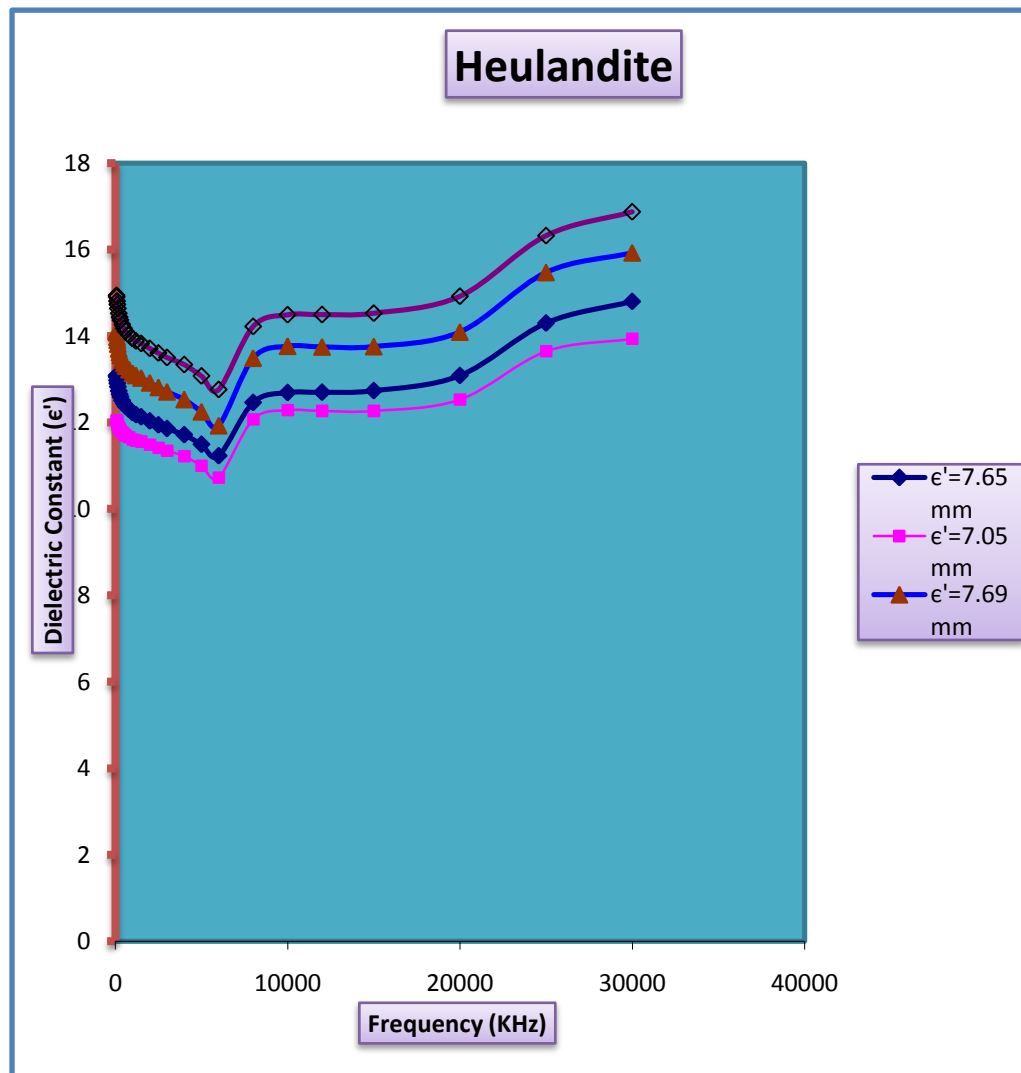


Fig. 5 variation of dielectric constant as frequency in Heulandite

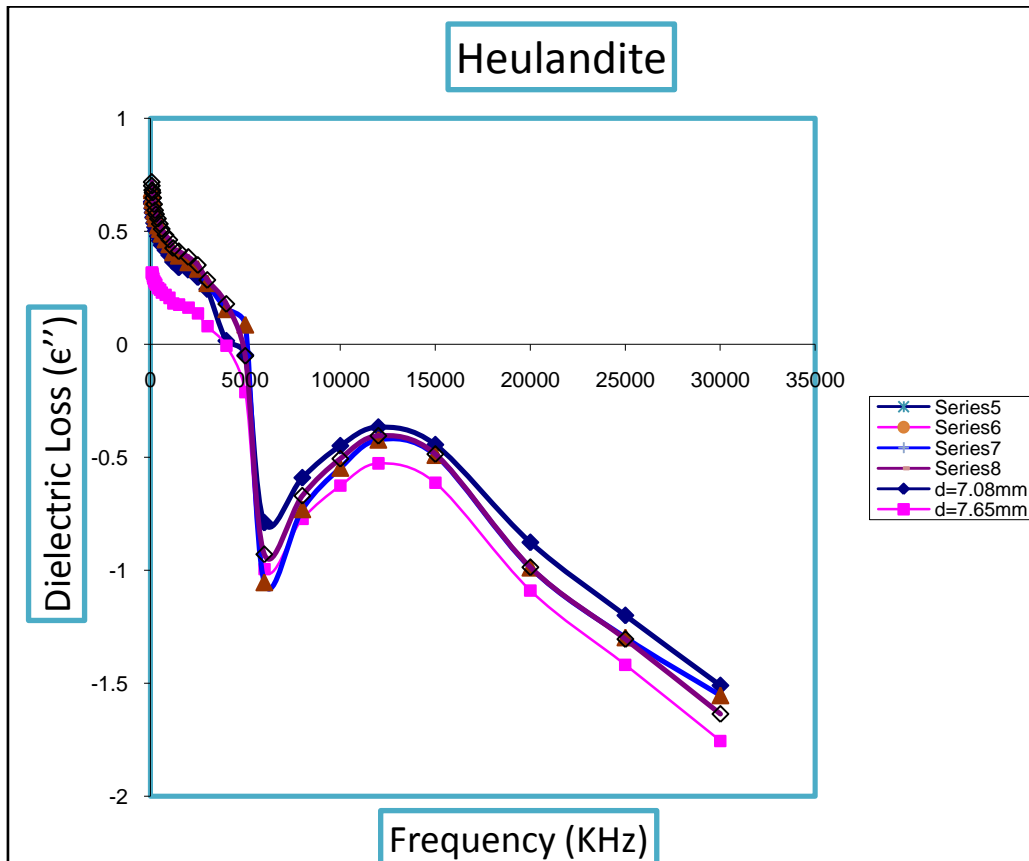


Fig. 6 variation of dielectric loss as frequency in Heulandite

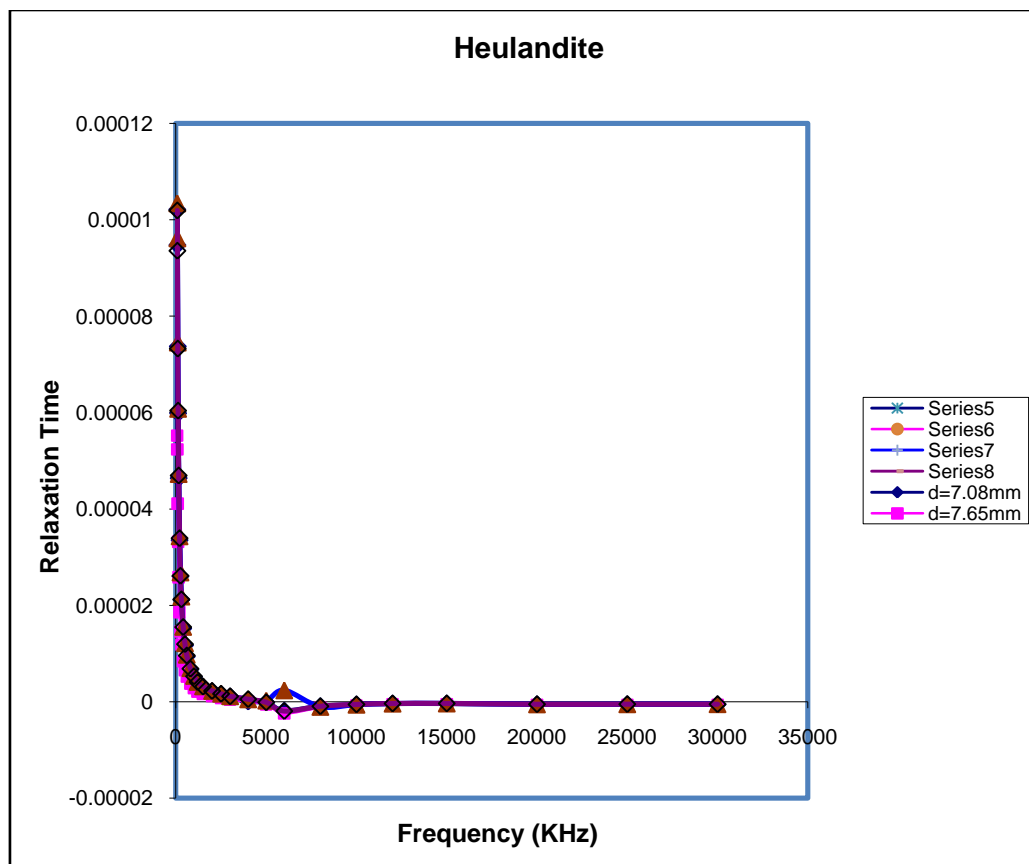


Fig. 7 variation of relaxation time as frequency in Heulandite

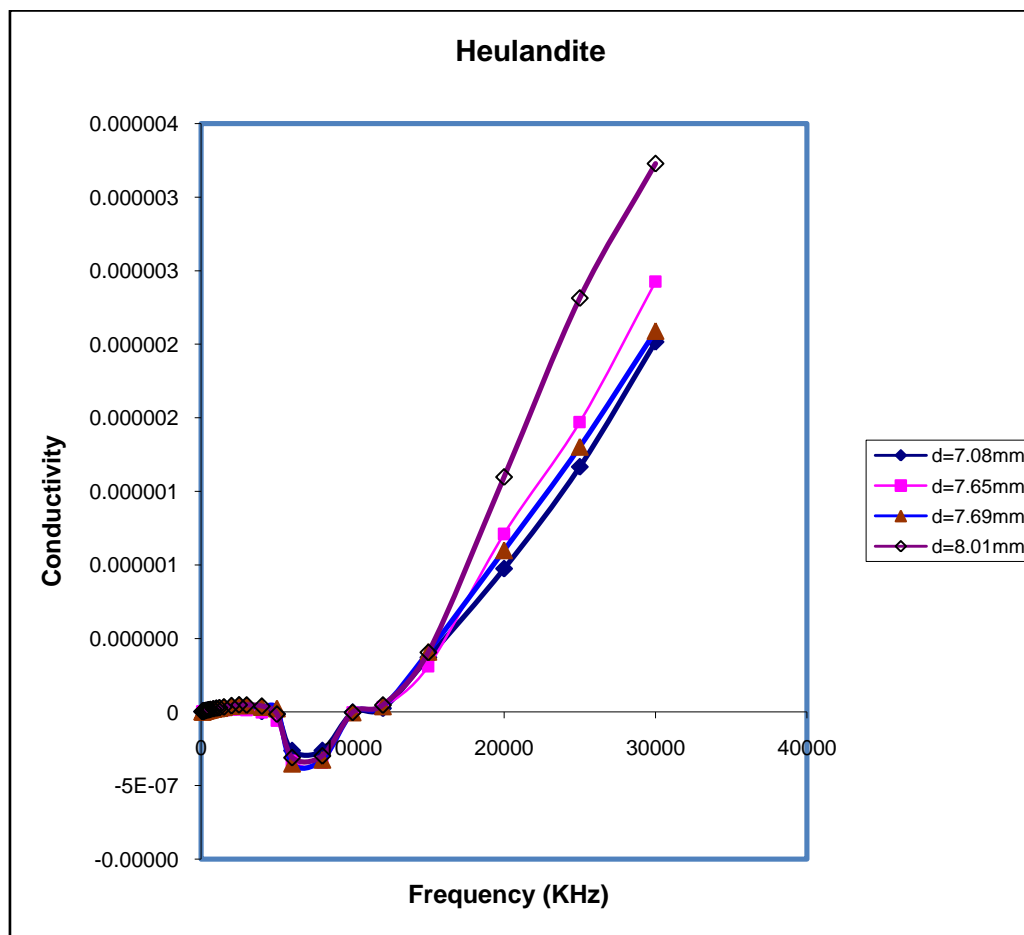


Fig. 8 variation of conductivity as frequency in Heulandite

VI. CONCLUSIONS

- 1) There is no major change in XRD Pattern of three forms of Heulandite
- 2) IR bands confirm the stability of Heulandite.
- 3) Dielectric study of Heulandite plays an important role in stating the nature of zeolite.

ACKNOWLEDGEMENTS

Author is thankful to Director of National Chemical Laboratory Pune for the support of characterization work. Director of CEDTI Aurangabad.

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