

Dielectric Study Of Zeolite Clinoptilolite

***Dr.V.P.Deshpande**

Shivaji college kannad

Dist.Aurangabad

Pin 431103

Prin.B.T.Bhoskar

Nutan mahavidyala sailu

Dist.Parbhani

Abstract :

Zeolite Clinoptilolite belongs to Group VII was collected near Ellora Ajanta belt. characterization was made using XRD, IR at NCLPune. Dielectric study was made using LCR Bridge. Pellets of Clinoptilolite were prepared, variation of dielectric constant, dielectric loss, dielectric conductivity and relaxsession time were measured from 20Hz to 20KHz of parent ,NH₄-Clinoptilolite and H-Clinoptilolite. Results were compared.

Keywords: Clinoptilolite,Characterization,Dielectric study

1 Introduction

Clinoptilolite is a silica rich zeolite that belongs to 7th group of platy zeolites(1). Heulandite, another platy zeolite of the same group and Clinoptilolite are isostructural but their thermal stability, Si /Al ratio and the cation contents are different. Boles(2) investigated the relationship between the chemical composition and thermal behavior of these zeolites and proposed the name of the zeolite as Clinoptilolite if Si/Al > 4 and if Si/Al < 4, the zeolite is termed as Heulandite. There are two varieties of Clinoptilolite, one silica rich is called as simply Clinoptilolite, whereas the low silica Clinoptilolite is known as ca-clinoptilolite(3)

The unit cell parameter of Clinoptilolite is

$$a= 17.62\text{\AA} , b=17.91\text{\AA} , c=7.39\text{\AA} , \beta=116^\circ , 18^\circ$$

The frame work structure of the Clinoptilolite consists of a common unit which contains 10 nodes, known as the 4-4-1 unit(4). These units are connected so as to share one or two nodes in zeolites. It is a monoclinic zeolite.

Clinoptilolite has been utilized intensively in environmental applications such as treatment of waste water from nuclear factories (5), remediation of radioactive soils (6), the treatment of sewage and agricultural effluents (7) etc. In such environmental applications, Clinoptilolite is valued for its high cation exchange selectivity for Cs , Sr and NH₄⁺ during ion exchange

As the Si/Al ratio increases for a group of zeolites ,the stability to acid attack also increases. The blocking effects of the cations in Clinoptilolite can therefore be minimized by the acid treatment, which reduces the cation exchange capacity by leaching Al⁺⁺⁺ from framework positions and substitutes H⁺ into the few remaining cation positions. Exchangeable cations are first replaced by hydrogen, followed by the hydroxylation of the Al-O bonds in the frame works, and the removal of ammonium from the framework into solutions . Acid treatment of several high silica natural zeolites produces a range of improved or modified sorbents both via , the mechanism of Dactionation and deallumination , and by dissolving any silica blocking channels in the structures by acid treatment on Clinoptilolite. surface area could be increased and effective pore size could be enlarged to allow the sorption of the benzene and isopentane . It also sorbs Kr, CO₂ and H₂O.

2 Sample Preparation

Clinoptilolite was collected from the quarries of Ajanta caves, Marathwada (Maharashtra). Sample was crushed and sieved to get 106 μm sized crystals for the ion exchanged. The sample was treated with 1 M solution of Ammonium Nitrate with stirring at 95°C. for the six hours. NH_4 ion exchanged form of Clinoptilolite is heated at 250°C for 48 hours for getting H – Clinoptilolite.

3 Characterization

X-ray diffraction patterns was recorded between 2θ values from 5° to 50° on Phillips model (PW 1710) with $\text{Cu K}\alpha$ wavelength= 1.54056 Å. Diffractogram are recorded for the parent Clinoptilolite, NH_4 – exchanged Clinoptilolite and H – form Clinoptilolite. D values & intensities are recorded in table 1

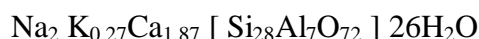
Infrared Studies:

The infrared spectra of Clinoptilolite was recorded on perkin – Elmer – 221 Spectrophotometer in the frequency range 400 – 4000 cm^{-1} of NH_4 – form, H – form & parent form at 100°C, 150°C and 200°C. The observed IR bands and assignments are given in table 2

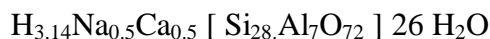
4 Chemical Formula

Chemical formula based on chemical analysis for Clinoptilolite is as follows

a) Parent form:-



b) H – form Clinoptilolite



5 Results and Discussion:

XRD – Pattern of the parent Clinoptilolite, NH_4 – exchanged Clinoptilolite and H – form Clinoptilolite is shown in fig.1. From diffractogram we determine the crystalline nature of Clinoptilolite d- values are compared with standard ‘d’ values. This confirms the Clinoptilolite structure. There is no major change in diffractograms of these three forms. The intensity in NH_4 – Clinoptilolite and H – form Clinoptilolite increases.

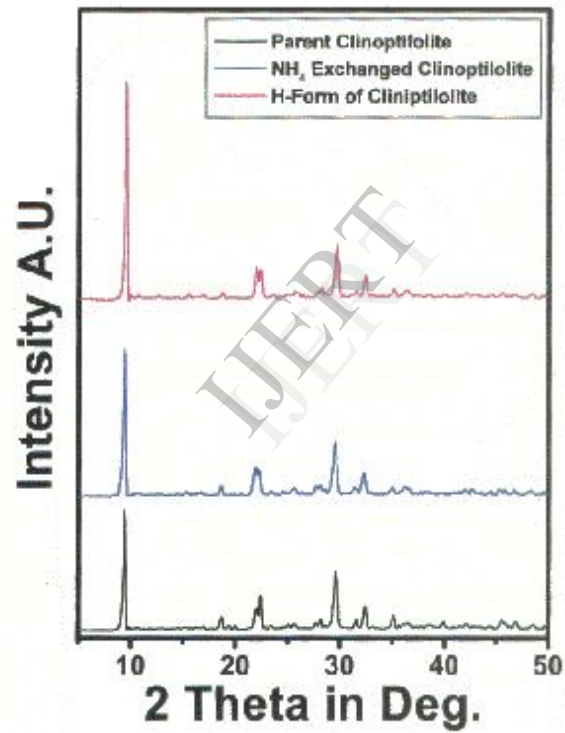


Fig 1 XRD pattern of clinoptilolite

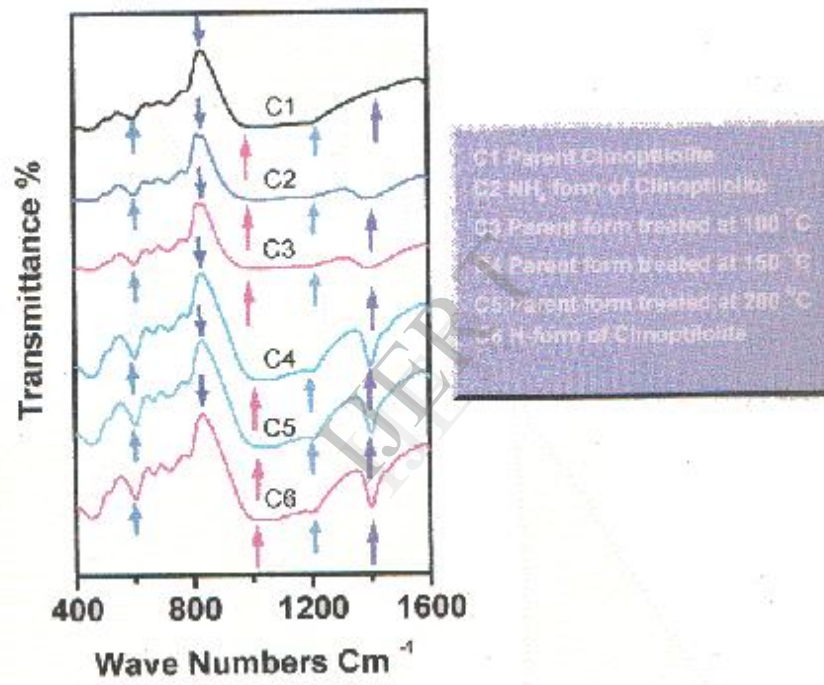


Fig. 2 IR of clinoptilolite from 400 - 1600

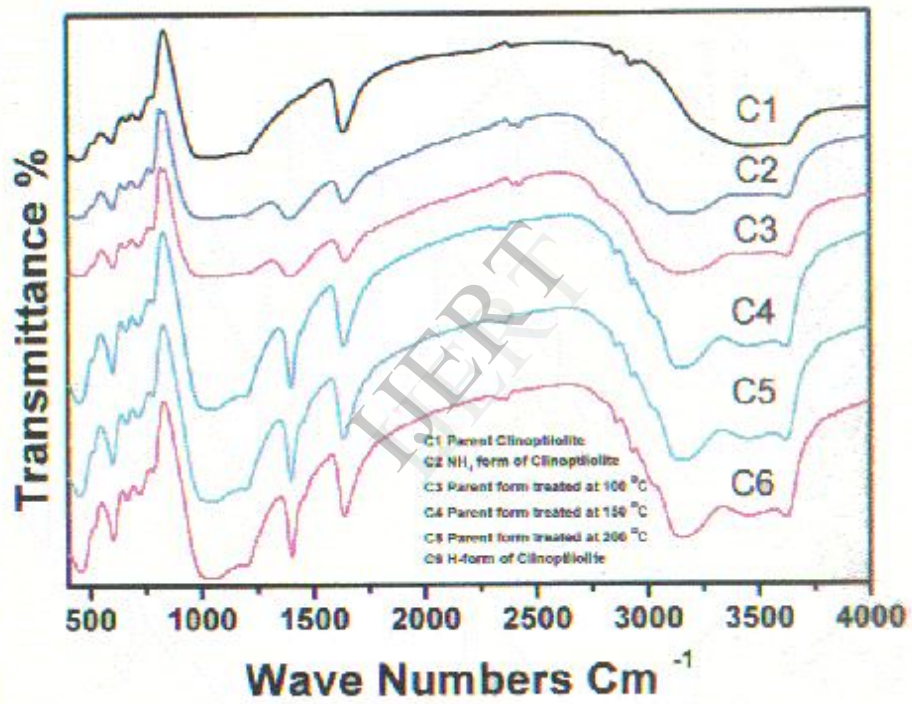


Fig. 3 IR of clinoptilolite from 400-4000

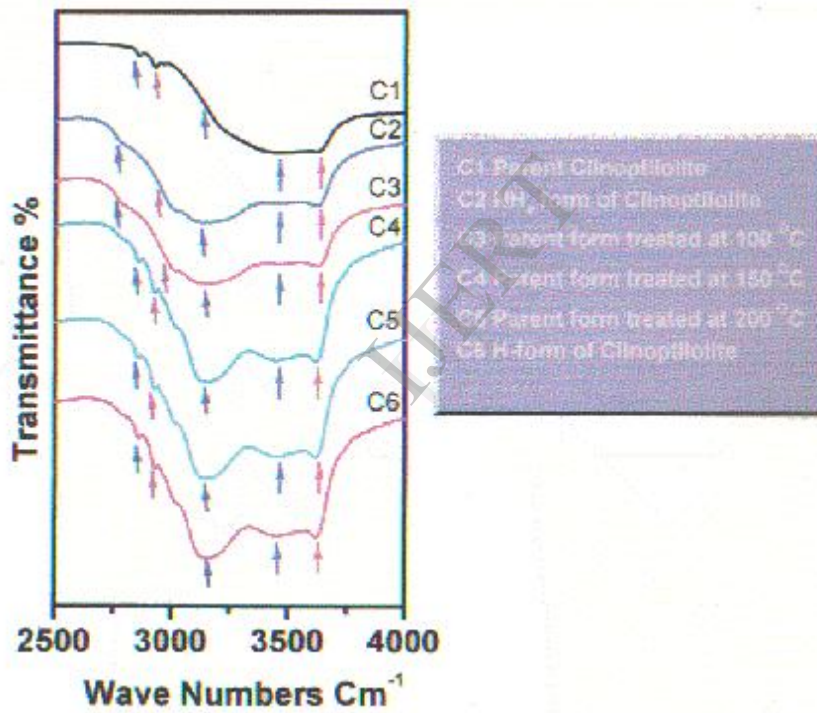


Fig. 4 IR of clinoptilolite from 2500-4000

2 Theta	d- Value	Peak Width	Intensity
09.91	08.93	0.12	100
16.64	05.33	0.06	1.3
19.11	04.65	0.06	6.4
19.83	04.48	0.12	1.9
22.28	03.99	0.16	3.7
22.75	03.91	0.16	3.8
23.84	03.73	0.24	0.9
25.46	03.50	0.16	1.2
28.54	03.13	0.16	1.5
29.95	02.98	0.12	15
30.23	02.96	0.16	7.3
31.95	02.80	0.16	1.8
32.89	02.72	0.28	2.7
35.52	02.53	0.20	1.6
40.28	02.24	0.16	2.6
42.47	02.13	0.24	1.1
44.67	02.03	0.64	0.4
45.97	01.97	0.24	1.5
47.27	01.92	0.32	0.6
48.96	01.86	0.40	0.4

Table .1- XRD Data For Clinoptilolite (After Background Subtraction)

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
Clinoptilolite	1391	772	598	1250	750	490	3625	1630

Table 2 IR assignments in Cm^{-1}

IR

IR spectra of heat treated zeolites provide new data concerning their dehydration and rehydration, the state of water, and the existence of hydroxyl groups and hydronium ion. The IR of Clinoptilolite and their ion exchange forms shows that depending on the radius, atomic number and valence of the exchange cations, change in the position of maxima and the intensities of high frequency bands takes place in the range of 400 to 4000 cm^{-1}

IR bands for Clinoptilolite are shown in table 2 in external linkage, asymmetric stretch is observed at 1391 cm^{-1} & symmetric stretch is at 795 cm^{-1} , OH- stretch is at 3625 cm^{-1} and the water bands are 1630 cm^{-1} . Double ring is observed at 598 cm^{-1} . Zeolite structure is insensitive to the asymmetric stretch at 1250 and symmetric stretch at 750 cm^{-1} bands at 490 is observed due to the vibration of Si - O or Al - O bond. As we heat the parent sample at 100°C, 150°C, 200°C & H - form Clinoptilolite there is no major change in IR spectrum this confirms the stability of the Clinoptilolite. Only water bonds become more intense and OH - stretching is more intense than the parent form of Clinoptilolite.

6 Dielectric studies of Clinoptilolite:

Dielectric study of material has been of considerable interest because of fast growth of mobile communication systems. Researchers have focused attention towards the development of materials with high dielectric constant which would allow the reduction of the size of resonators since the wave length (λ) of a dielectric resonator is inversely proportional to $\sqrt{\epsilon_r}$ where ϵ_r is the relative dielectric constant of the resonator

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 $90-\delta$, 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

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

Where $\omega = 2 \pi f$

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

Conductivity $\sigma = \omega \epsilon_0 \epsilon''$

6.1 Parent form Clinoptilolite

When a dielectric material is subjected to an alternating field the orientation of the dipoles and hence the polarization will tend to reverse every time the polarity of the field change. As long as the frequency remains low the polarization follows the alternations of the field without any significant lag and the permittivity is independent of the frequency and has the same magnitude as in a static field. When the frequency is increased the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations will begin to lag behind those of the field. As the frequency is further raised the permanent dipoles, if present in the medium, will be completely unable to follow the field and the contribution to the static permittivity from this molecular dipoles, the orientation polarization ceases. This usually occurs in the radio frequency range of the electromagnetic spectrum. At still higher frequencies, usually in the infra-red the relatively heavy positive and negative ions cannot follow the field variations so that the contribution to the permittivity from the atomic or ionic polarization ceases and only the electronic polarization remains. The above effects lead to fall in the permittivity of a dielectric material with increasing frequency a phenomenon which is usually referred to as anomalous dielectric depression.

Dispersion arising during the transition from full atomic polarization at radio frequencies to negligible atomic polarization at radio frequencies to negligible atomic polarization at optical frequency is usually referred to as resonance absorption. Dispersion arising during the transition from full orientational polarization at zero or low frequencies to negligible orientational polarization at high radio frequencies is referred to as dielectric relaxation.

Dielectric constant:- The variation in ϵ' with frequency is shown in the fig 5 decrease in ϵ' is observed up to 6000 KHz. Then it increases suddenly up to 8000 KHz. Then it increases slowly or remains nearly constant. The dielectric constant ϵ' increases with the increase in the sample thickness.

Dielectric Loss (ϵ'') : -The variation of ϵ'' with frequency is shown in the fig 6. A decrease in dielectric loss ϵ'' was observed with increase in frequency up to 4000 KHz. Loss is decreasing slowly and then decrease is on fast negative side again. Loss increases up to 10,000 KHz. Then it decreases. As thickness increases dielectric loss increases.

Relaxation time (τ):- The variation of τ with the frequency is shown in fig 7. Relaxation time decreases as frequency increases.

A.C. Conductivity (σ):- The variation of A.C. conductivity against frequency is shown in fig 8. It was observed that as frequency increases conductivity goes on increasing and as thickness increases the conductivity goes on increasing.

6.2 NH_4 ion exchange Clinoptilolite

Dielectric constant (ϵ'):- The variation of the NH_4 ion exchange Clinoptilolite against frequency is shown in fig 9. Decrease in dielectric constant is observed up to frequency 5000 KHz. Then ϵ' increases slowly or nearly remain constant. Also observed that dielectric constant increases with increase in thickness of the sample

Dielectric Loss (ϵ''): Fig 10 shows that the variation of ϵ'' against frequency decrease in ϵ'' with increase in frequency is observed

Relaxation Time :- Fig 11 shows the variation of relaxation time against the frequency. There is decrease in (τ) as the frequency increases.

A.C. Conductivity:- Fig 12 shows the variation of conductivity against frequency as frequency increases the conductivity goes on increasing, initially σ increases up to 5000 (KHz). Then decreases up to 6000 (KHz). Then increase linearly as thickness increase the σ goes on increasing.

6.3 H – Form Clinoptilolite

Dielectric Constant:- Fig 13 indicates the variation of dielectric constant against frequency in H – form Clinoptilolite Decrease in dielectric constant up to

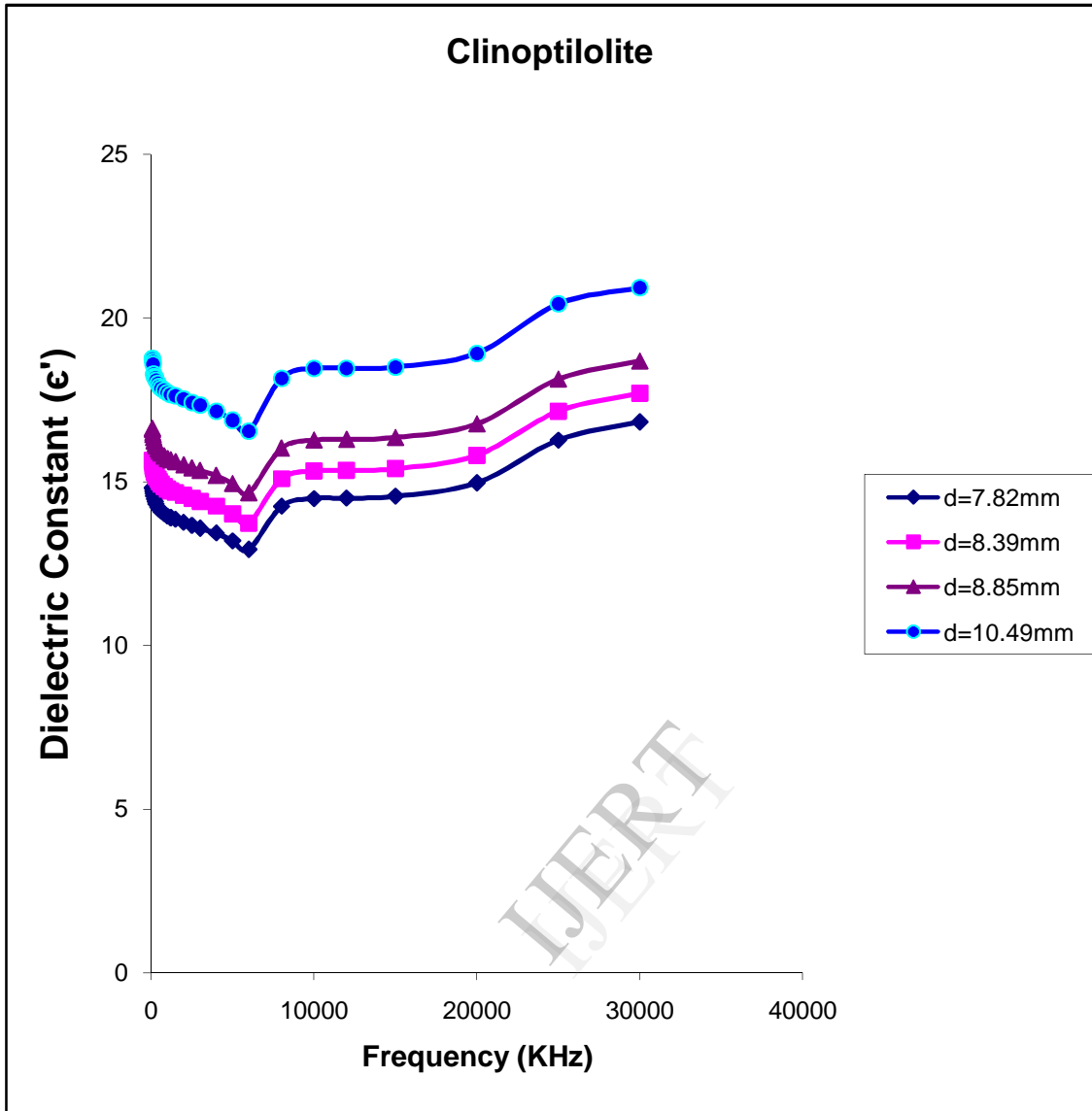


Fig. 5 Variation of dielectric constant as a frequency in clinoptilolite

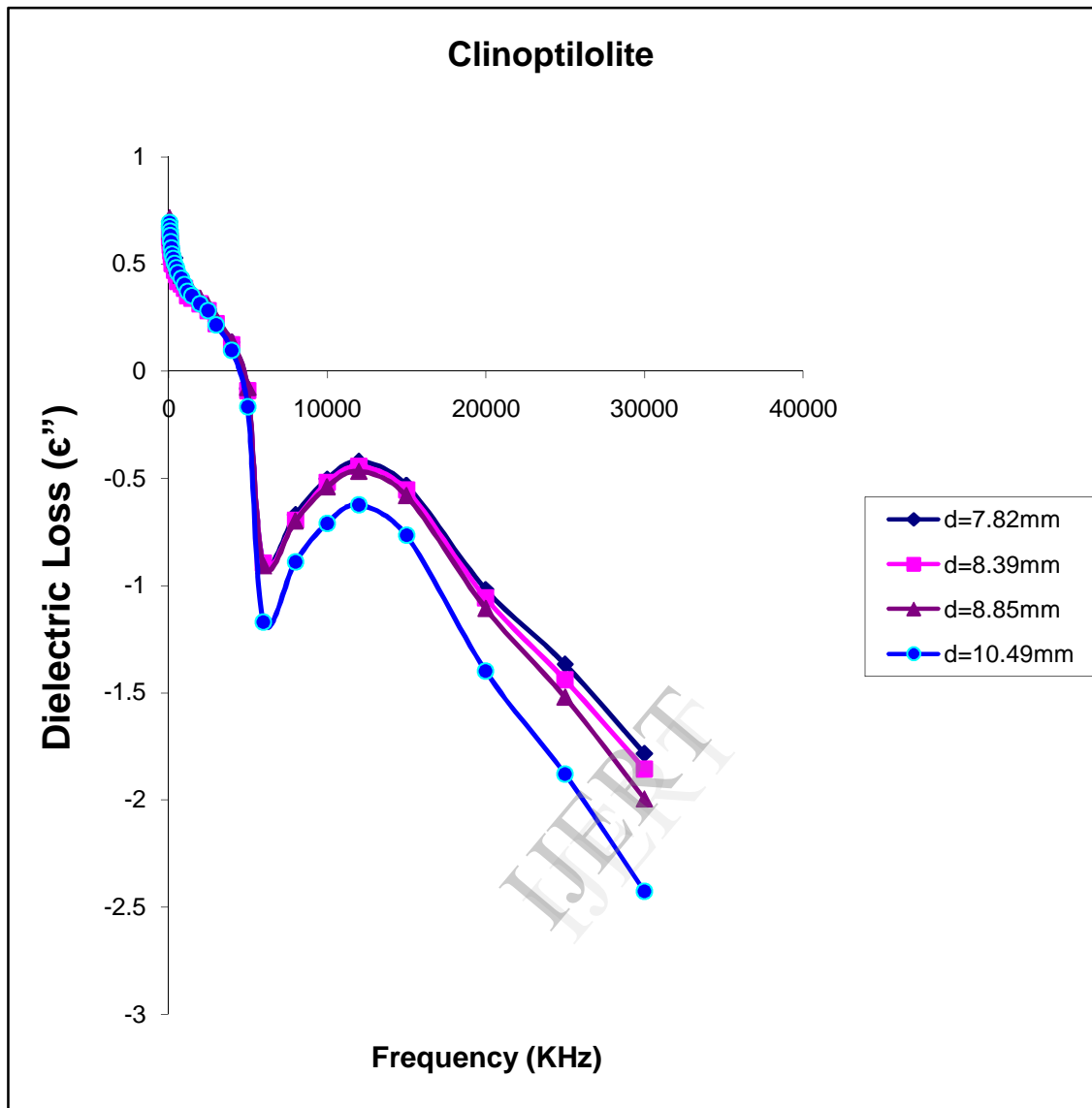


Fig. .6 Variation of dielectric loss as a frequency in clinoptilolite

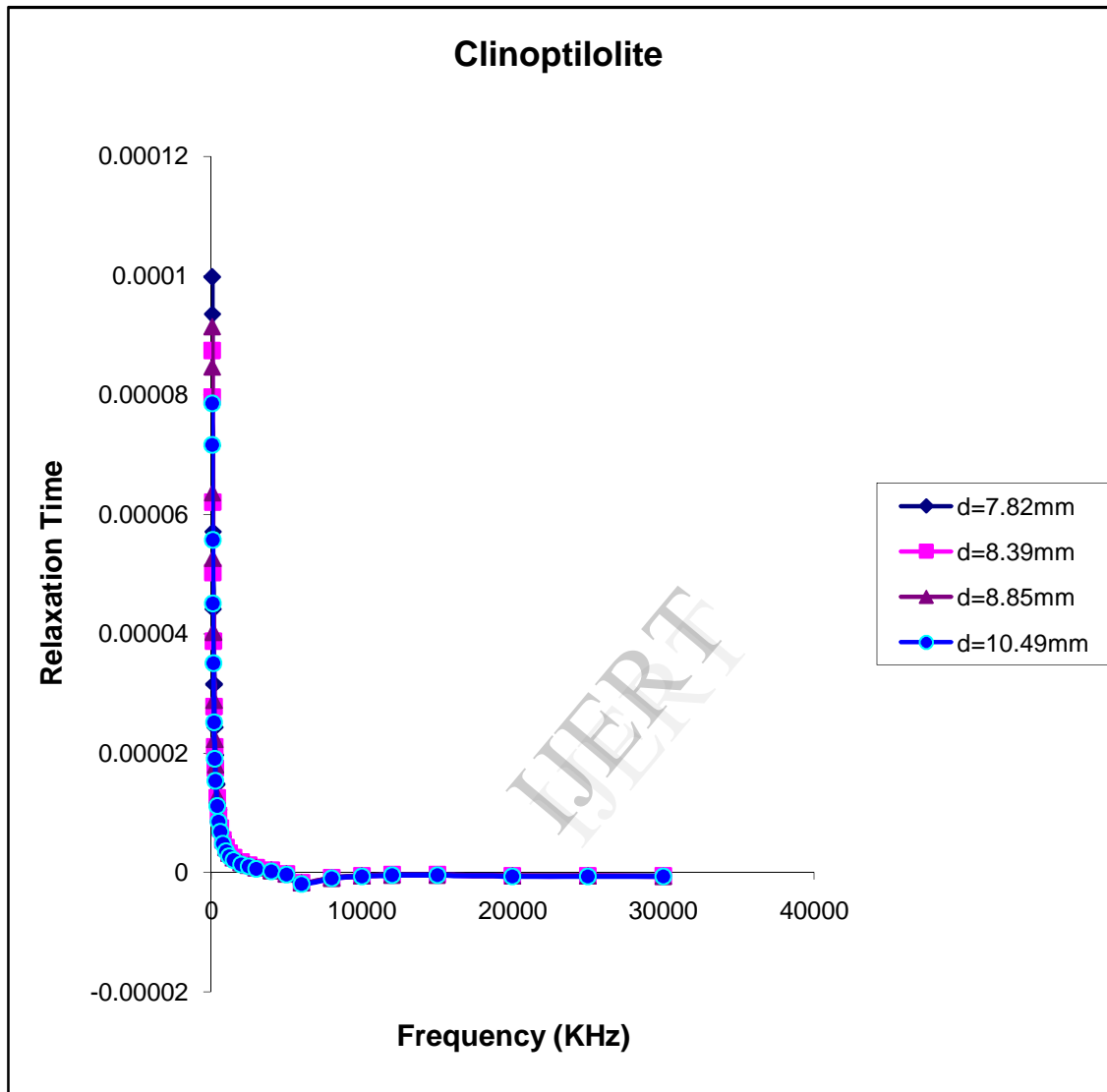


Fig. 7 Variation of relaxation time as a frequency in clinoptilolite

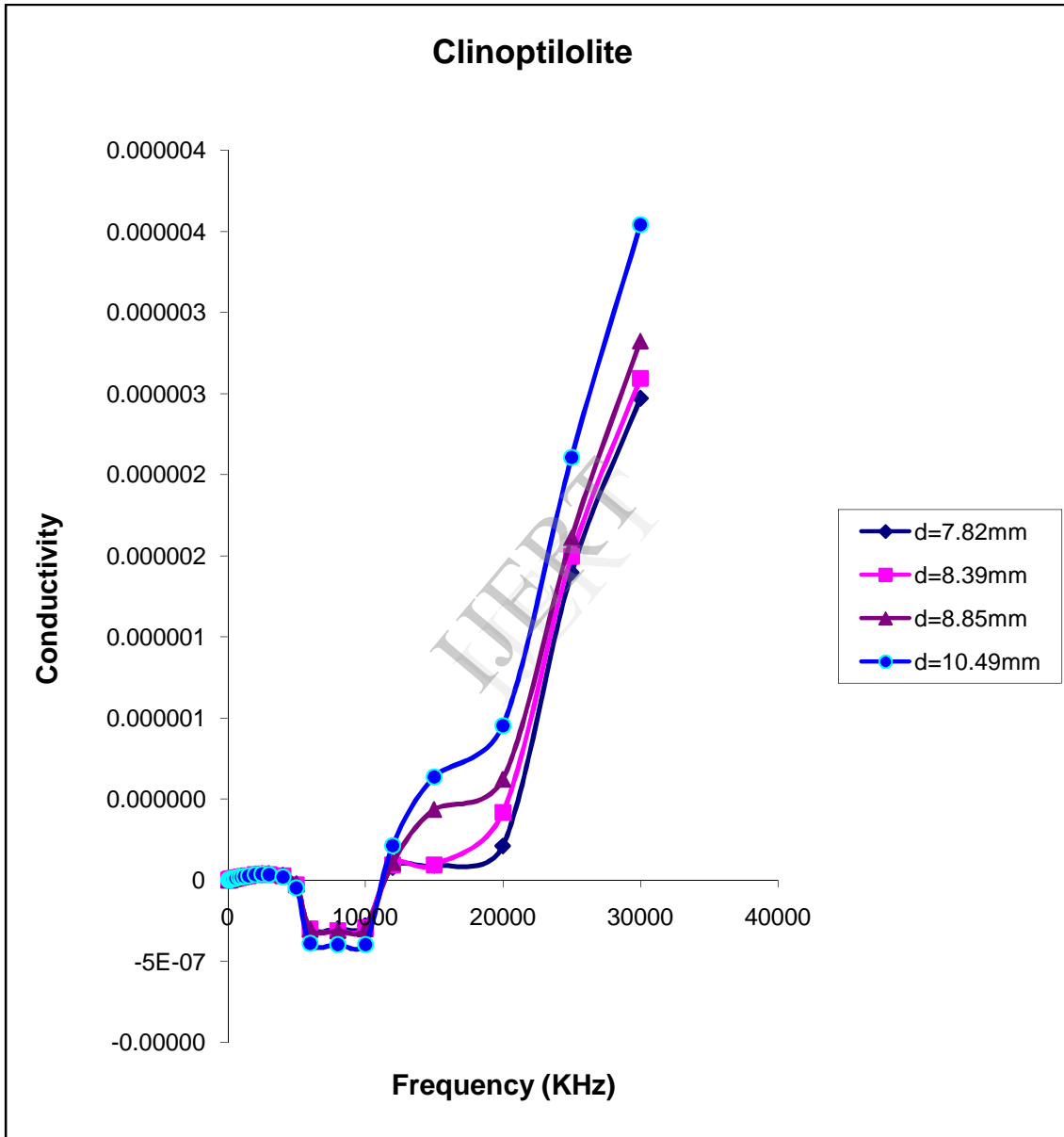


Fig.8 Variation of conductivity as a frequency in clinoptilolite

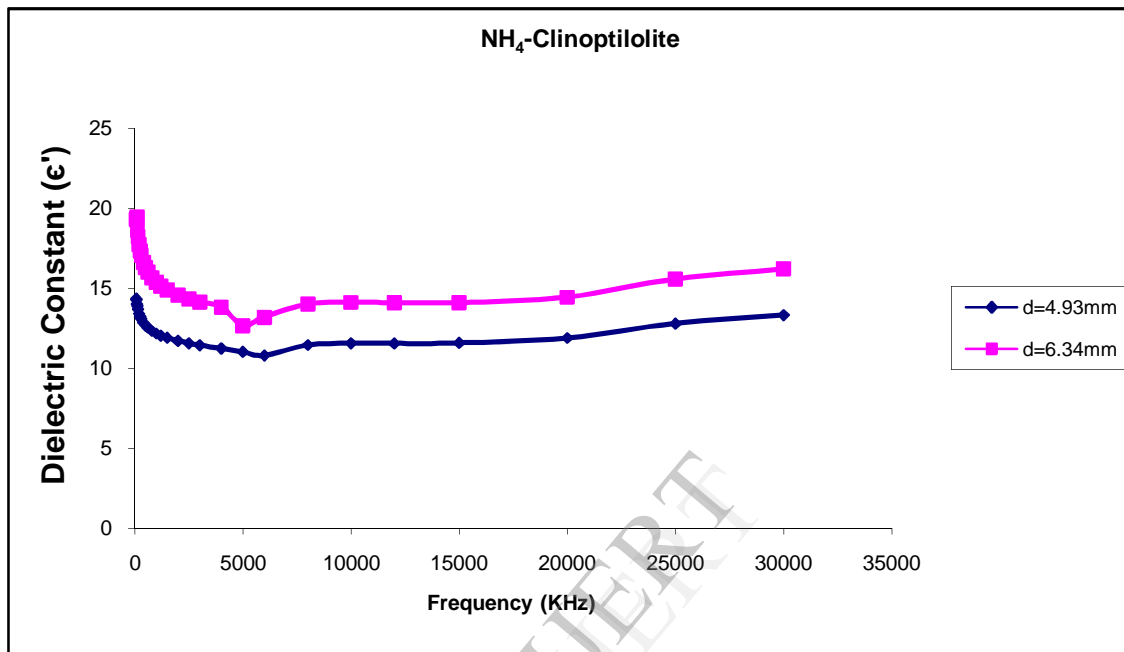


Fig..9 Variation of dielectric constant as a frequency inNH₄ clinoptilolite

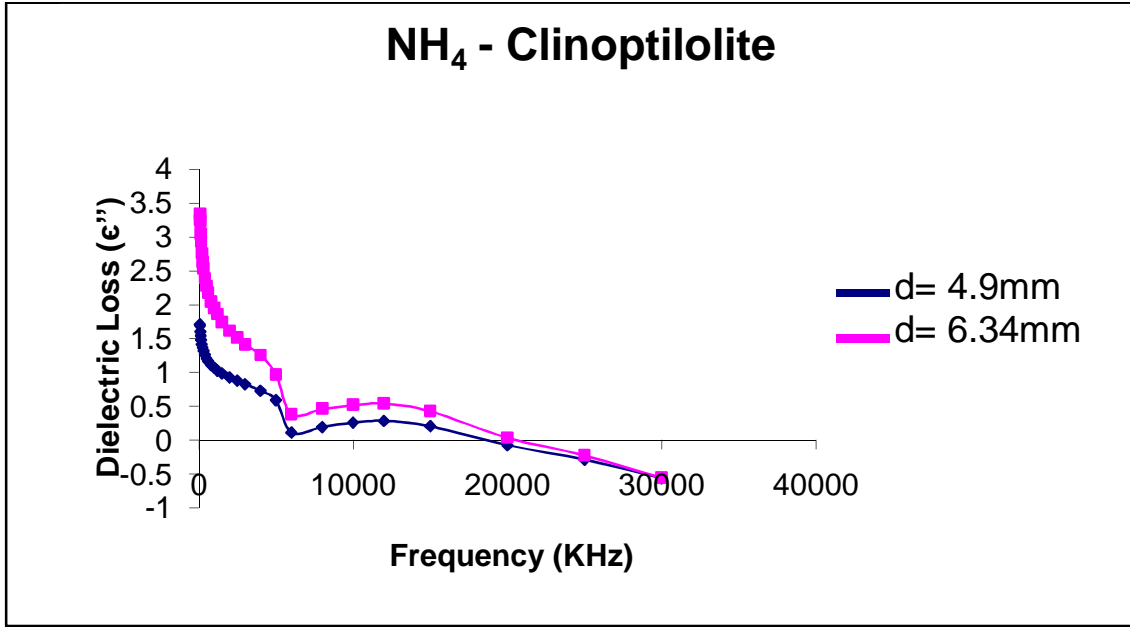


Fig. 10 Variation of dielectric loss as a frequency in NH_4 clinoptilolite

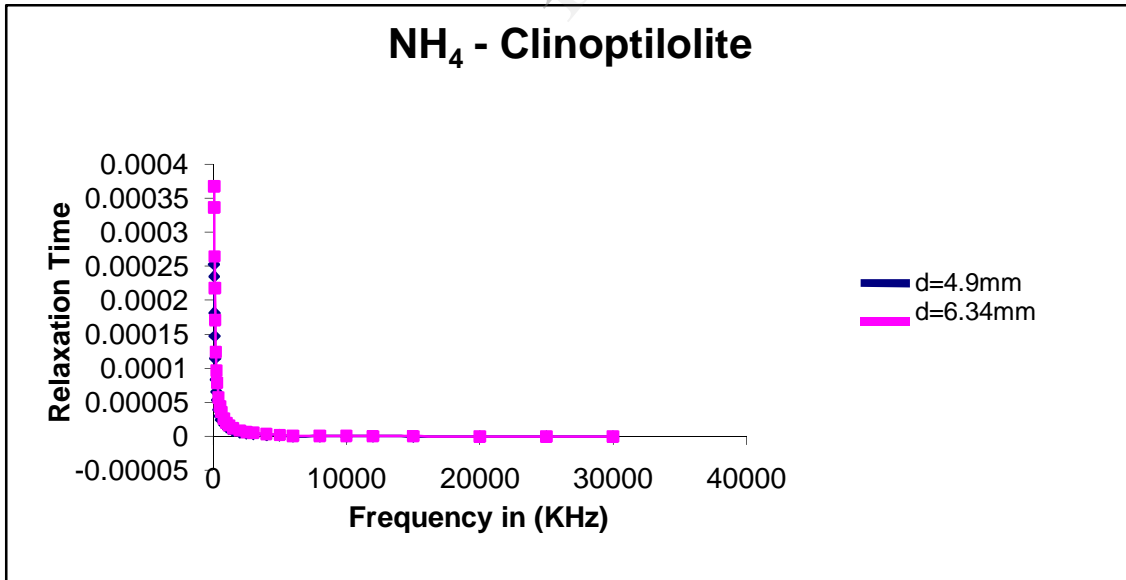


Fig. 11 Variation of relaxation time as a frequency in NH_4 clinoptilolite

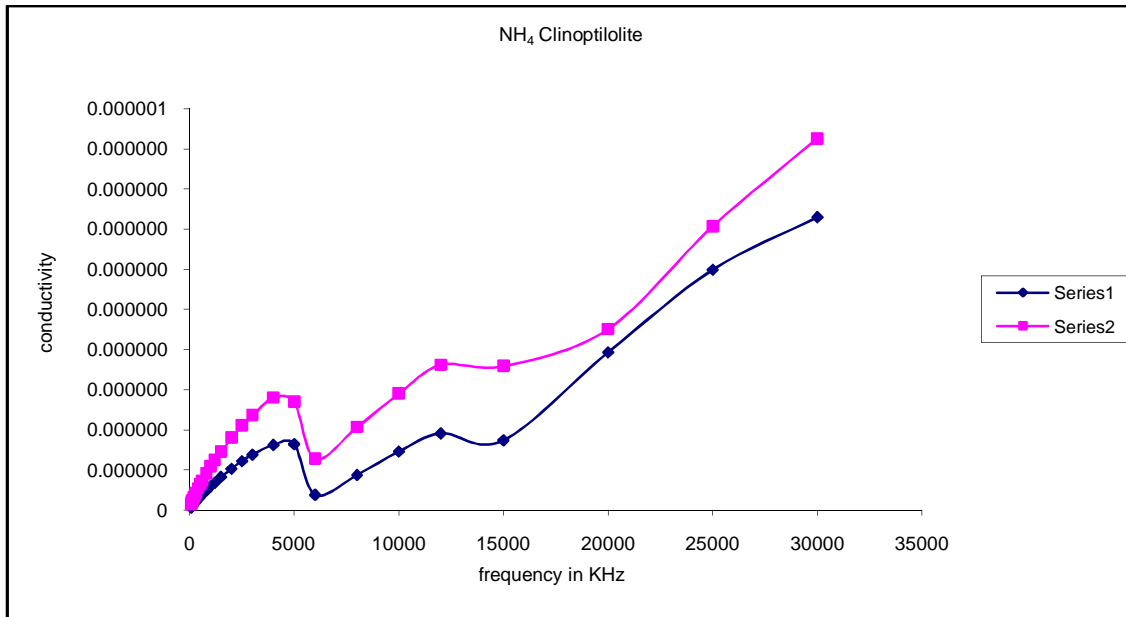


Fig. 12 Variation of conductivity as a frequency in NH₄ clinoptilolite

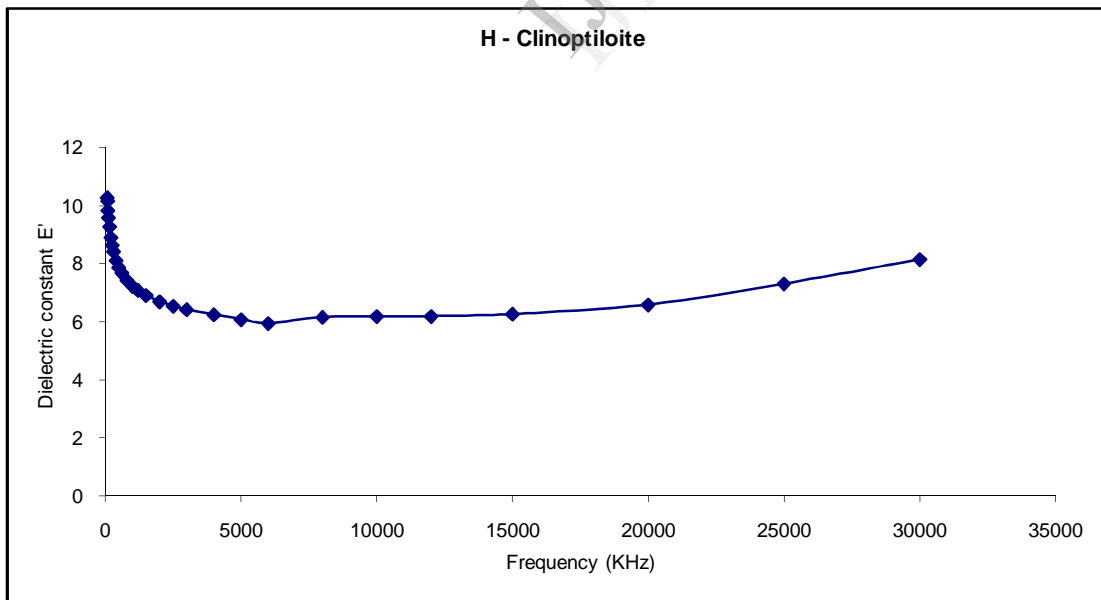


Fig. 13 Variation of dielectric constant as a frequency in H clinoptilolite

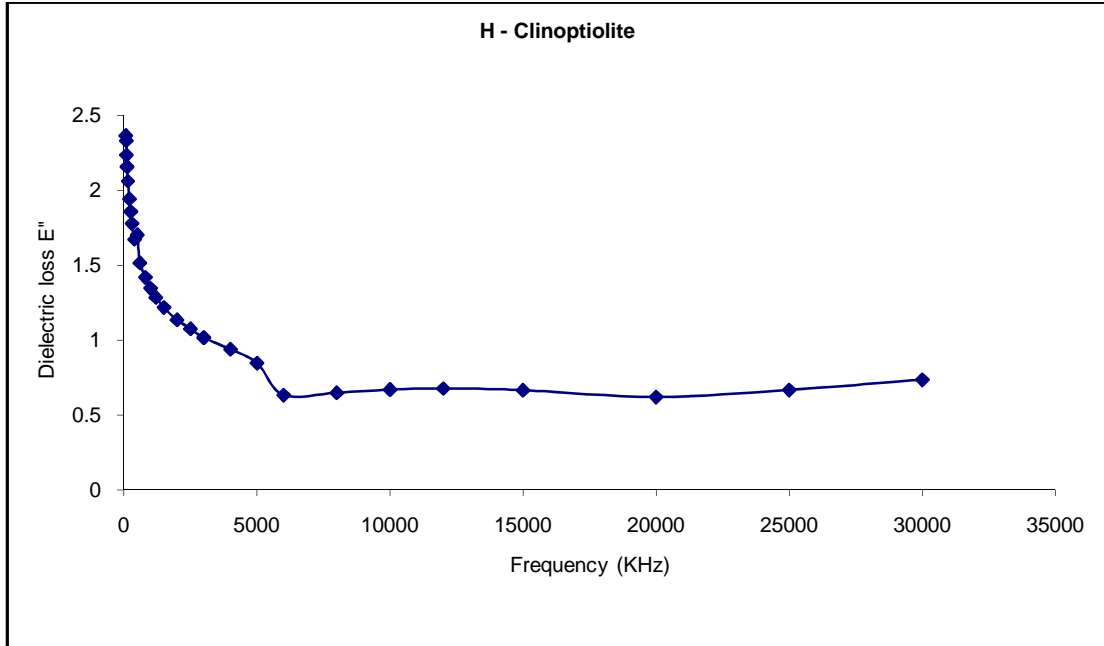


Fig. 14 Variation of dielectric loss as a frequency in H clinoptilolite

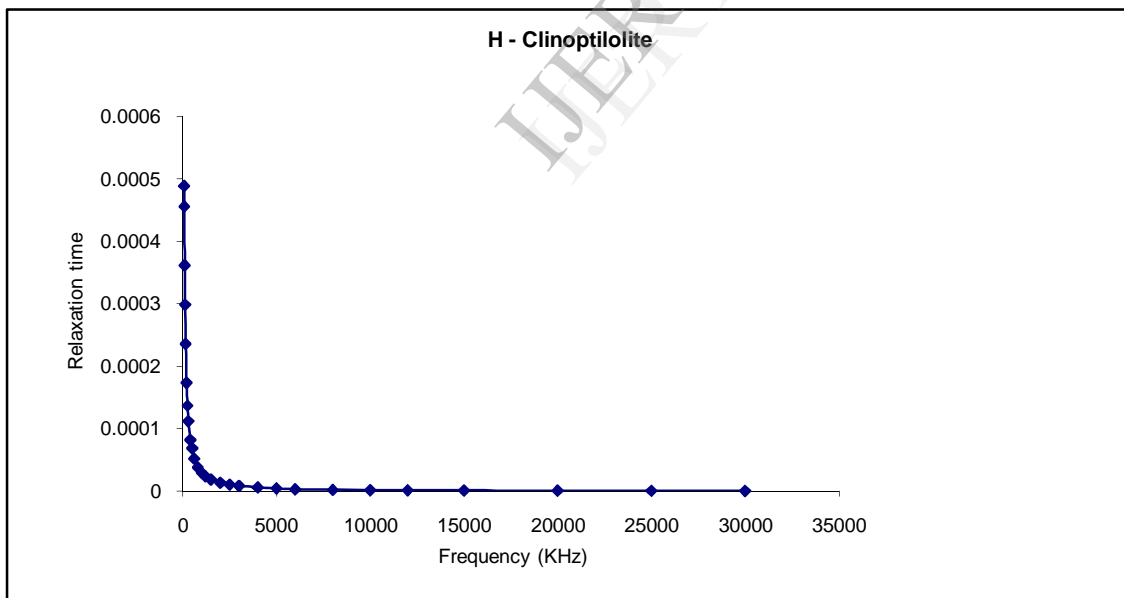


Fig. 15 Variation of relaxation time as a frequency in H clinoptilolite

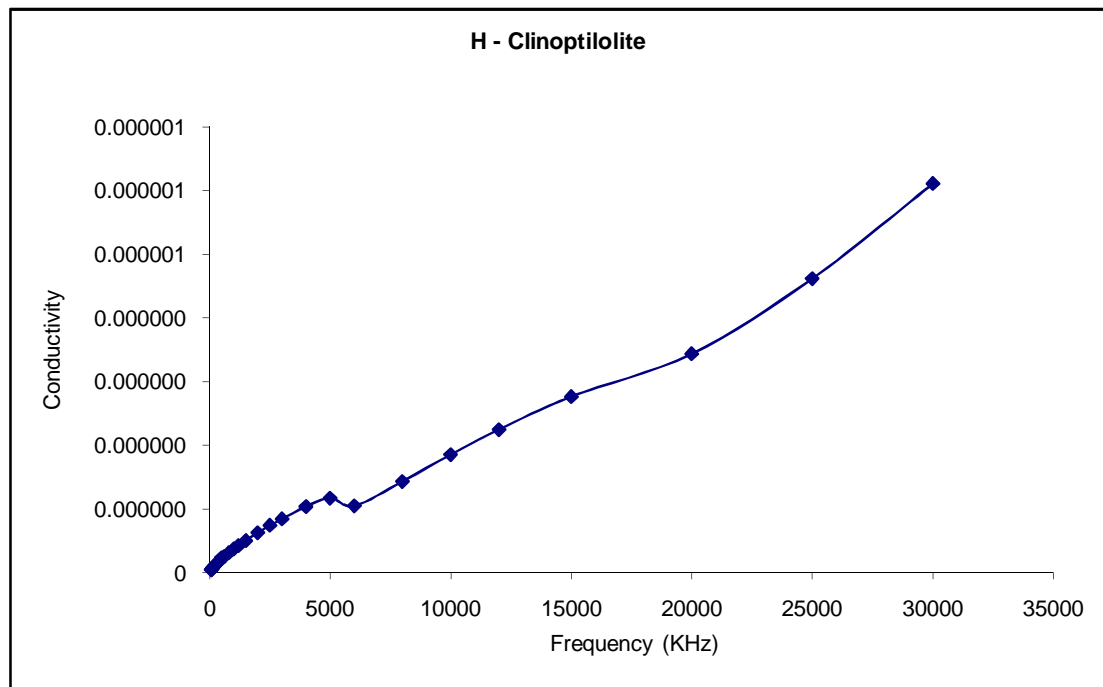


Fig.16 Variation of conductivity as a frequency in H clinoptilolite

000 KHz is observed. Then dielectric constant slowly increases or nearly remains constant.

Dielectric Loss (ϵ'') :- Fig 14 shows the variation of dielectric loss to the frequency. This shows that decrease in ϵ'' is observed as increase in the frequency up to 5000 KHz. Decrease is fast. Then ϵ'' is remain constant.

Relaxation Time (τ) :- Fig 15 shows the variation of relaxation time with frequency. This shows that decrease in τ is observed in H- Clinoptilolite as increase in the frequency.

A.C. Conductivity (σ) :- Fig 16 shows the variation in AC Conductivity with frequency. From fig. 6 conductivity goes on increasing as frequency increases linearly.

7 Conclusions

- 1) There is no major change in XRD Pattern of three forms of Clinoptilolite .
- 2) IR bands confirm the stability of Clinoptilolite,
- 3) Dielectric study of Clinoptilolite plays an important role in stating the nature of zeolite.
- 4) From chemical analysis we conclude that there is no structural change in zeolite by ion exchange & H – form of zeolite except cation exchange.

Acknowledgements

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8 References

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