Ion Exchange And Dielectric Study Of Mordenite

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Abstract:

Zeolite Mordenite 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. Pellets of Mordenite were prepared, variation of dielectric constant, dielectric loss, dielectric conductivity and relax session time were measured from 20Hz to 20KHz of parent Mordenite,NH4-Mordenite and H-Mordenite.Results were compared.

Keywords: Mordenite,Characterization,Dielectric study

1 Introduction

Zeolites of the Mordenite group are stable to high temperature. Mordenite is one of the natural zeolites abandoned enough for commercial exploitation, and the synthetic varieties have been used for two decades. Zeolites structures have been classified on the bases of secondary building units. Structure types assigned to the Mordenite group can be built from 5-1 units consisting of the single 5 ring and attach tetrahedron. The structure of Mordenite was determined by Meier(1961) and consists of chains of 5 membered rings parallel to C axis connected through double eight membered rings in the AC plane . These are joined to give 12 ring channels in the Sea direction. With double 8 ring prisms lining the channel in the AC plane as adjacent 8 ring prisms are offset about 3.7 A° in the sea direction (C/2) , the path between the 12 ring channels is very distorted 8 ring having a minimum free diameter of about 2.8 A° .Early studies of Mordenite showed that assist to the structure was limited to molecules having a diameter of less than 4.2 A°.

Meier explained this by proposing that faulting occurs parallel to the   [001] plane in the [010] direction. Such displacements replaces the 12 ring diffusion part by an 8 ring part and produces a structure consistent with much of the sorption data of the natural Mordenite. The compositions of the Mordenite fall within a narrow Si/Al range of 4.4 to 5.5 and generally have calcium and sodium as the major cations . The high Si/Al ratio make this one of the most thermally and acids stable zeolites. Mordenite can be readily deactionated and dealluminiated by acid solutions which are of the particular interest as catalysts and catalytic promoters. To differentiate between Mordenite having 12 member ring channels and those having 8 channels sand (1968) proposed the generally accepted terms large port and small port. Natural mordenites are small port. Synthetic varieties may be either small or large port depending on synthesis conditions and washing procedures. Many small port varieties can be converted to large port form by acid treatments or ammonium exchange. Recent work on ammonium Mordenites indicates that these dealluminate like acid treated Mordenite .

Early sorption experiments on Mordenite show that the mineral rapidly sorbs NH_3 and CO_2 and O_2, N_2 and Ar but sorption of CH_4 and C_2H_6 is very slow . Sorption capacity is generally increased in going from the sodium to H form. The high Silica to Alumna ratio of Mordenite make them interesting sorbents for acidic gases . Sodium and H Mordenite are good sorbents for HCL and NH_3 respectively. Several investigations have shown that

Mordenite have the acid stability, selectivity and capacity to SO_2 and SO_3 from stack gases sorb NO_2 commercial availability of the synthetic large port Mordenite was a major stimulus to hydrocarbon sorption research on Mordenite.

Mordenite is a zeolite with an ideal composition $Na_8[(AlO_2)_8(SiO_2)_{40}]24H_2O$. It's structure is orthorhombic with unit cell parameters a=18.11 A° , b=20.46 A° and c= 7.52A° [1]. The aluminosilicate skeleton consists in parallel elliptical channels with 12 or 8 ring apertures. The main channels are interconnected by a small side channels. Mordenite is a naturally occurring silica rich zeoliote (Si/Al ~ 5). The Si/Al ratio in a Mordenite is an important factor for it's thermal stability and reactivity [2].

Large deposits of Mordenite are present as sediments in the ocean and in saline alkaline lakes. In zeolitized tuffs Mordenite content sometimes reaches 70% and more. Si/Al − ratio is reasonably at the constant 4.5-5.5. Exchangeable cations are represented by the calcium and sodium in different ratios; potassium and magnesium are present in small amounts. This chapter deals with the dielectric properties of Mordenite.

2   Sample Preparation

The zeolites under the study were collected from the quarries near Ajanta and Ellora caves. Ion exchange in zeolites is usually a relatively simple task. The alteration in the composition of the cations may produce some remarkable change in zeolite properties. For present studies we use three form

1) Original Mordenite
2) NH_4 ion exchange Mordenite
3) H –Mordenite

The freshly extracted crystals were separated from the geodes. Then crushed and sieved to get 106 μm sized crystals. The powdered sample was washed repeatedly with distilled water to remove soluble impurities and dried. The as grown sample was treated at 95° C for six hours in 1 M solution of Ammonium Nitrate (NH_4NO_3) with a solid solution ratio of 1:15 with stirring. After washing with distilled water filtering and drying at 80° C for the several hours the ion exchanges sample were obtained. The samples so obtained were used to study the Physicochemical properties.

NH_4 ion exchange form of Mordenite is heated at 250 °C for 48 hours & obtained H-Form of Mordenite.

3   Characterization

3.1 **X-ray Diffraction** :- The X-ray diffraction were recorded between 2θ values ranging from 5° – 50° with a chart speed of 1 /min on a Phillips x- ray diffractometer (model PW 1710 BASED) and Ni filtered having wavelength CuKα radiation (λ= 1.54056 A°). Continuous scan type was used for the analysis of the samples. The x-ray diffractograms are recorded for parent Mordenite, NH_4 exchanged Mordenite and H-form Mordenite in fig 3.1 the relative intensities and 'd' values compared with standard 'd' values reported and are given in table 3.1

3.2 Infrared Studies:- The IR spectra of parent Mordenite, NH_4 form and H form of Mordenite were recorded on a Perkin – Elmer – 221 spectrophotometer in the frequency range 400 to 4000 cm^{-1} using Nujol Mill technique. The parent Mordenite at the temperature 100, 150 and 200 °C were recorded on the same model

The observed infrared bands and assignment are given in table 3.2. Structure sensitive , structure insensitive and the water bands are compared with the reported data (3) which confirms the framework structures of these zeolites.
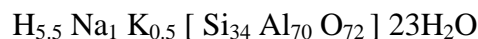
4   Chemical Formula

The chemical analysis was carried out by wet chemical analysis method. The chemical formula obtained from chemical analysis of Mordenite is as follows:

In parent form

$$Na_4 K_3 [Si_{34} Al_7 O_{72}] 23 H_2O$$

In H – form

$$H_{5.5} Na_1 K_{0.5} [Si_{34} Al_{70} O_{72}] 23H_2O$$

5   Dielectric Studies

For the dielectric studies, Mordenite of parent form , NH_4 ion exchange and H –form was taken in pellets form of different thickness. Pellets are formed under the pressure of 8 tones. The electrode polarization could be reduced greatly by improving the electrode contacts with the silver pest pressed on the pallets. The powder samples of Mordenite were

treated with Polyvinyl Alcohol (PVA) and then pelletized at a pressure of 8 tones. The dielectric properties were measured on pellets (Coated with Ag Paste as electrodes). Using the observation were close to each other and the values were averaged.

Frequency range 75KHz to 30 MHz is applied between two sides of pellets and measure the capacity value and by knowing this value we calculate Dielectric Constant. Dielectric Loss, A.C. Conductivity and Relaxation Time of Parent form, NH_4 ion exchanged form and H- form of Mordenite.

6 Results and Discussion

The physical perfection is equally important after the identity and quantity of the atoms present in a crystal, for crystal characterization. The beginning of such work is the accurate determination of structure of crystals with X-rays. These techniques, based on monochromatic X-radiation are generally more important because the d-spacing can be calculated from the observed diffraction angles. For natural zeolites and synthetic zeolites, x-ray powder diffraction methods are commonly used for the structural investigations and also for the purpose of identification.
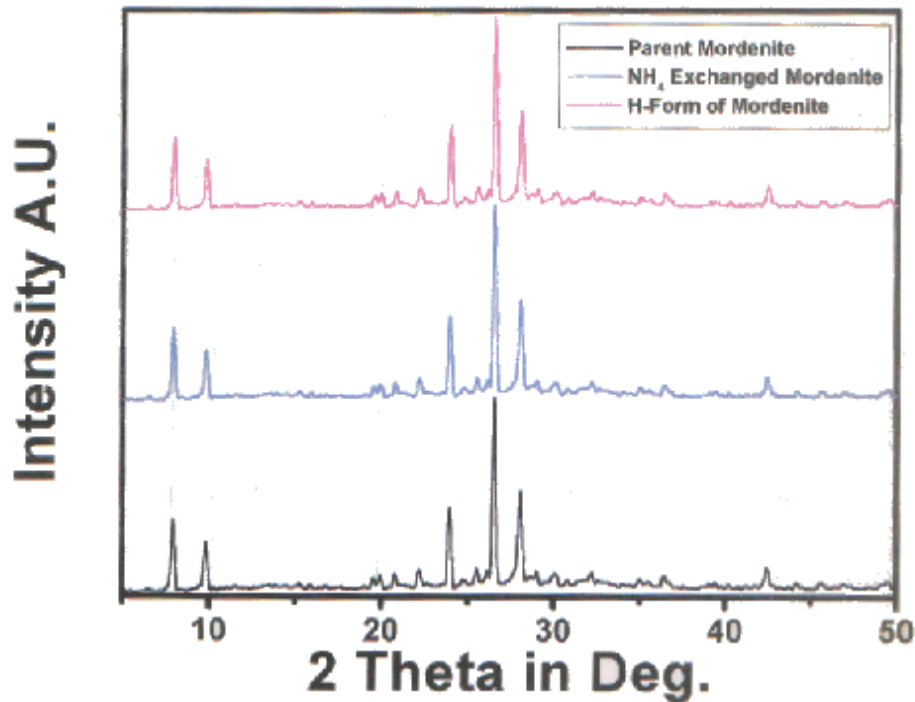
Fig 1.1 XRD Pattern of mordenite

In the present investigation, the bragg diffractometer arrangement is used. The specimen in the form of micro crystalline powder is mounted in the sample holder, which is then placed at the center of the diffractometer and rotated   by an angle θ around on axis in the sample plane. The counter is attached to an arm rotating around the same axis by angles twice as large as those of the specimen rotation only (hkl) planes of the microcrytals parallel to the sample plane contribute to the diffracted intensity.

From the diffractogram of parent Mordenite, NH_4 exchanged Mordenite and H –form of Mordenite there is no change except intensity. This shows the stability of material 'd' values are compared with standard 'd' values (4) .This confirms the Mordenite zeolite. Change in intensity is due to the difference in scattering factor of cations (5).

The d values from the X-ray powder diffraction patterns for zeolite samples are given in table 3.1   It was found that in most of the cases the d values agree fairly well with the standard d values given in ASIM data cards. From the lattice parameters this confirms the orthorhombic structure of mordenite.

2)Infrared Studies :-

By an extension of the infrared studies, it may be possible to deduce structural information on a new zeolite for which x-ray structural analysis is not complete. The object of this study is to apply mid-infrrared spectroscopy to zeolite structural problems with the help of using infrared, as a tool to characterize the frame work structure and to detect the presence of polyhedral building units present in zeolite frameworks.
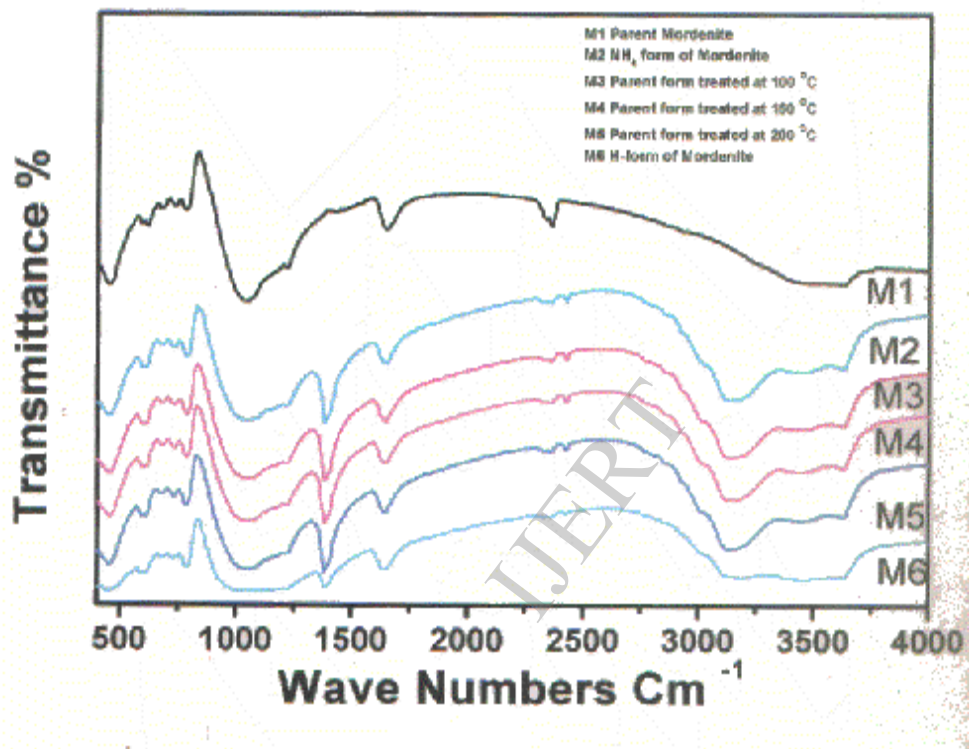

Fig 1.2 IR of mordenite

Infrared spectrum in the region 400 to 4000 cm^{-1} is sensitive tool indicating structural features of zeolite frame works. It can also be said that the major structural group present in zeolites can be detected from their infrared pattern. There are often general similarities among the spectra of zeolites with the same structural type and in the same structural group. The infrared spectra of zeolites in the region 1300 – 200 cm^{-1} appears to consists of two classes of vibrations.

1) Those due to internal vibrations of the TO_4 tetrahedron which is the primary unit of structure. These vibrations are not sensitive to variations in framework structure

2) Vibrations which may be related to the linkages between tetrahendra. are sensitive to the framework structure and to the presence of some SBU and building block polyhedra such as double rings and the large pore openings.

In Particular, zeolite structures have been studied by IR spectroscopy (6). For natural zeolites, spectroscopic data are more scanty, although some Japanese workers have examined the IR spectra of the eight natural zeolites. These investigations have yielded information on structural properties, the state of the adsorbed phase and effects of various types of treatment. Structural characteristics of zeolite lattice obtained by IR studies of certain zeolites in the range of aluminosilicate skeleton frequencies (200 – 1300 cm^{-1}) have been reported (7). Oscillations of the zeolite frame work in the range 200 to 1200 cm^{-1} have been classified as being either structure sensitive oscillations of external tetrahedral bonds or structure insensitive oscillations of individual tetrahedra on the basis of this classification and with wide ranging experimental evidence, the bands were described to modes: antisymmetric stretches (1250 – 9500cm^{-1}) Symmetric stretches (720 – 650 cm^{-1}) and deformations (490 – 500 cm^{-1}) modes involving the external bonds include double ring (650 – 500 cm^{-1}) poreopening (300 – 420 cm^{-1}) symmetric (750 – 820 cm^{-1}) and antisymmetric stretching frequencies (1050 – 1150 cm^{-1}). Studies of the IR spectra of Mordenite showed that they are characterized by the absorption bands at 550 – 650 , 650 – 720 , 750 – 820, 850 – 900 , 1000 – 1100 and 1150 – 1250 cm^{-1} (8). These bands arise from vibrations of the Si-O (Al) and Al-O(Si) bonds in tetrahedral combined in the aluminosilicate oxygen frame work vibrations of the Si-O (Al) bond caused by the internal deformations (symmetric and antisymmetric) are revealed at 650-720 , 780-820 and 900-1250 cm^{-1}. The most intense bands are observed at 1040-1100. The band at 750-820 cm^{-1} is clearly caused by symmetric vibration of the Si-O bond. The adsorption bands at 550-650-cm^{-1} relate to oscillations of chain of aluminosilicate oxygen tetrahedral.

2 Theta	d – Value	Peak width	Intensity
05.41	16.34	0.48	44

9.97	8.88	0.12	58
13.85	6.40	0.48	2
19.67	4.51	0.16	13.5
20.05	4.43	0.16	18.4
20.82	4.27	0.40	6.5
22.26	4.00	0.20	17.5
24.12	3.69	0.12	40
24.92	3.57	0.20	9.4
25.73	3.46	0.12	12.8
26.67	3.34	0.12	100
28.17	3.17	0.08	64
29.08	3.07	0.08	7.5
30.05	2.97	0.48	7
30.98	2.89	0.24	6
32.31	2.77	0.16	2.8
35.25	2.55	0.48	4.2
36.52	2.46	0.16	6.5
39.02	2.31	0.16	15
42.03	2.15	0.48	2
44.34	2.04	0.64	1.5
45.79	1.98	0.12	6.5

Table 1.1- XRD Data for Mordenite (After Background Subtraction)

IR of Mordenite from 400 to 4000 cm^{-1} are recorded for different conditions i.e. parent form (M1) NH$_4$ form (M2) parent form at 100 °C (M3) parent form at 150 °C (M4) parent form at 200 °C (M5), H – form (M6) and assignment of bands are shown in table 3.2.

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$0 Bands
Mordenite	1227	785	625	1057	773	459	3625	1625

Table 1.2 IR Assignment of Mordenite

In the external linkage (structure sensitive) Asymmetric stretch is observed at 1227 cm^{-1} and symmetric stretch is observed at 785 cm^{-1}, Hydroxyl stretch is observed at5 3625 cm^{-1} and the water bands are 1625 cm^{-1}. Double ring is observed at 625 cm^{-1}. Zeolite structure in internal tetrahedral structure (insensitive) , asymmetric stretch is at 1057 cm-1 and symmetric stretch is at 773 cm^{-1}, bands at 459 cm^{-1} are present due to vibration of Si-O or Al-O bond after NH$_4$ treatment to the parent zeolite and heating the sample at 100 °C, 150

°C, 200 °C & H – form of zeolite not major change in the bands which confirms the stability of Mordenite after ion exchange and heating up to H-form band at 3615 cm^{-1} is due to the OH – stretch this band is more intense in H-form than original form bands at 2846 cm^{-1} , 3000 cm^{-1} & 3115 cm^{-1} are observed due to hydroxyl stretching bands in the region 900 cm^{-1} to 1200 cm^{-1} are observed due to skeleton vibration of Si-O , O-Al-O bond.

Dielectric Study of mordnite :

Dielectric study of material has been of considerable interst   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 $\sqrt{\varepsilon_r}$ where ε_r is the relative dielectric constant of the resonator

Dielectric constant :

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

$\varepsilon' = C.d / A. \varepsilon_0$

where d = thickness of the pellet

A = area of pellet

ε_0 = premitivity 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 90^0 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 permitiivity in a complex form as

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

Where ε^* is the complex relative permittivity

ε'' is the measure of the heat related loss in the material

Current in capactor Tan $\delta = \varepsilon''/ \varepsilon'$

Dielectric relaxation:

It is defined as decay of polarization with time 10^{-12} to 10^{-10} second. It occur 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 $T = \varepsilon'' / \omega\varepsilon'$

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 $\sigma = \omega\varepsilon_0\varepsilon''$

WHERE $\omega = 2\pi F$

a) Dielectric constant Є' (Parent form): - The plot of the dielectric constant Є' with frequency is shown in fig 3.5. The dielectric constant was found to decrease with increase in frequency up to 6000 KHz. At first dielectric constant is more because of space charge polarization. The dielectric constant increases suddenly at 7000 KHz then it remains constant up to 20,000 KHz and increases slowly up to 30 MHz. . Dielectric constant decreases because of relaxation due to changing frequency. Dielectric constant increases because of the interfacial polarization

Further it was also observed that the dielectric constant Є' increases with the increase in thickness of the sample.

b) Dielectric Loss (Є'') :- Fig 3.6 shows the variation in dielectric loss Є'' against frequency .The dielectric loss was found to decrease with increase in frequency dielectric loss decreases rapidly up to frequency 4000 KHz. It goes to negative value up to 12000 KHz it again increase up to 15000 KHz then decreases.

c) Relaxation time (т):- Fig 3.7 shows the variation in Relaxation time against frequency. Relaxation time goes on decreasing with increasing frequency. Relaxation time remained nearly constant with change in sample thickness.

d) A.C. Conductivity:- The fig 3.8 shows the variation of conductivity as a function of frequency . The conductivity almost increased with in increase in frequency. The conductivity was also found to increase with increase in the thickness of the sample.

NH$_4$ Mordenite

Dielectric Constant:- Є'

1) **Dielectric constant Є':-**Fig 3.9 shows the variation of dielectric constant against frequency of the ion exchange form of Mordenite. The dielectric constant decreases up to 6000 KHz and in creases from 8000 KHz and remain nearly constant. Further increase with increase in thickness of the sample. At first dielectric constant is more because of space charge polarization.

2) **Dielectric Loss (Є'')**:- Fig 3.10 shows the variation of the dielectric loss against frequency of NH4 Mordenite. The dielectric loss goes on decreasing with increase in frequency, it decrease up to 6000 KHz and increases up to 15000 KHz then decreases. Dispersion in dielectric loss is due to the space charge polarization a peak in ε'' also occurs at one frequency since the most energy is dissipated at that point
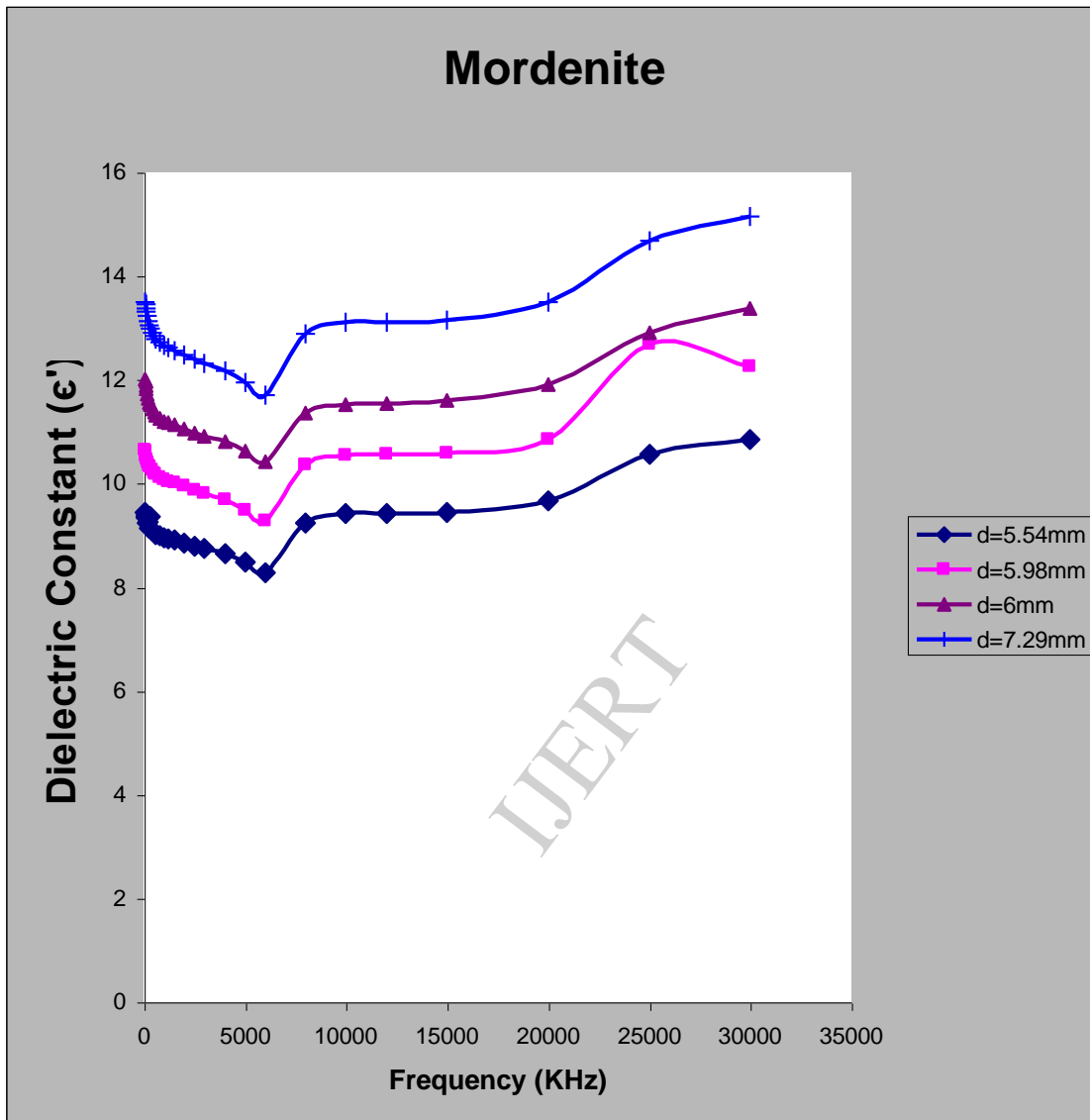
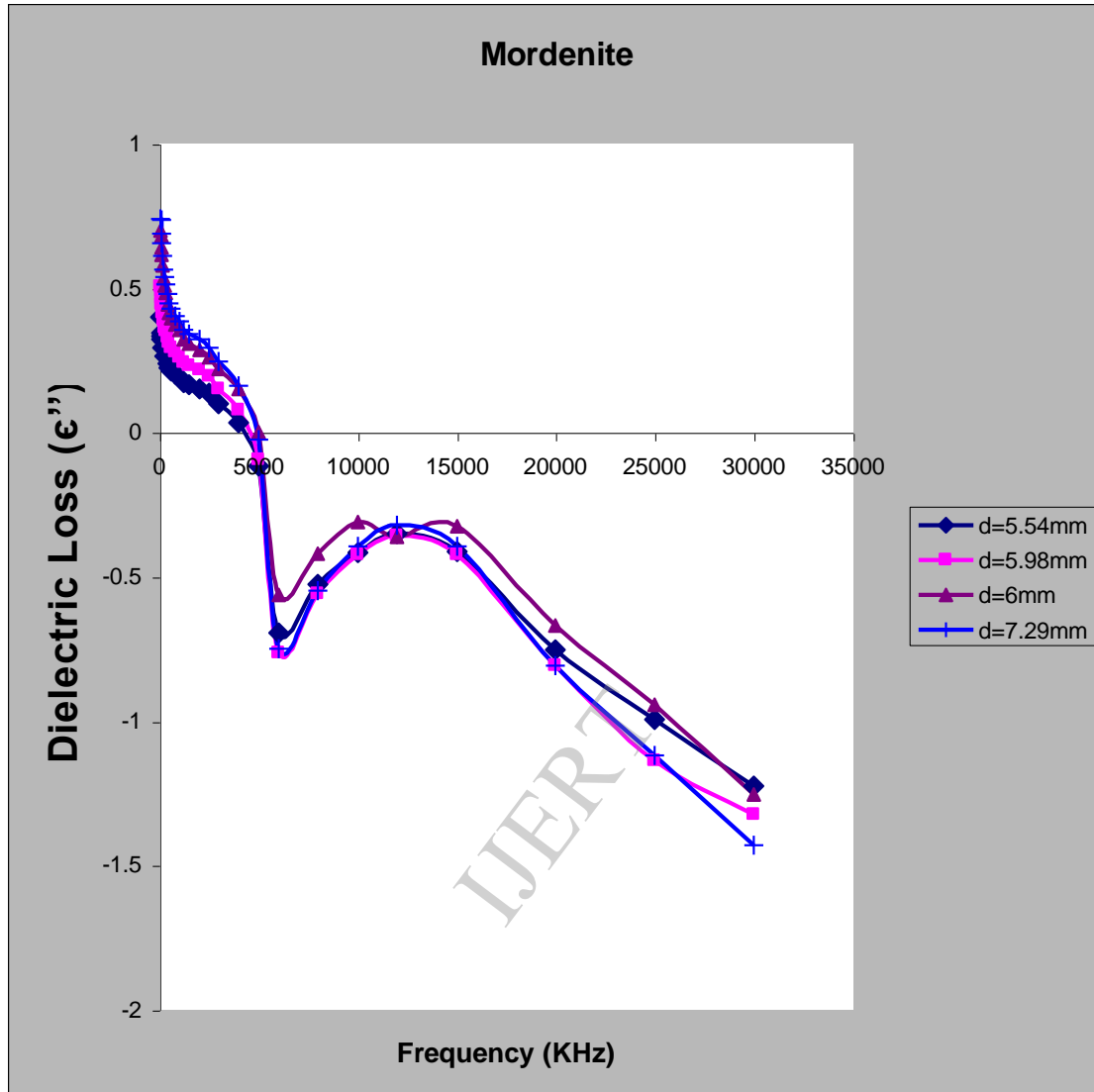*Fig1.5 Variation of dielectric constant as a frequency*
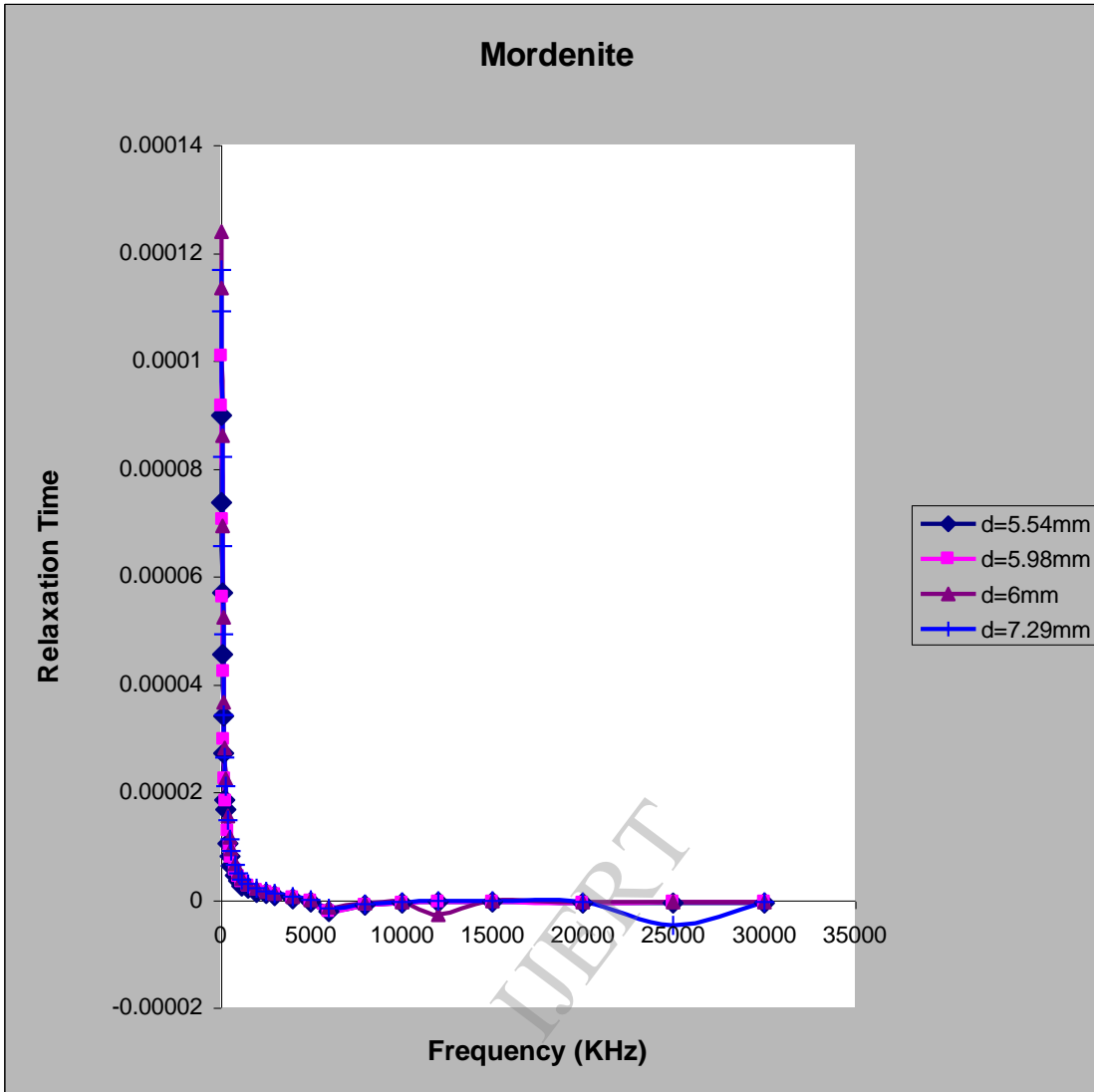
Fig. 1.6 Variation of dielectric loss as frequency

Fig.1.7 variation of relaxation time as frequency
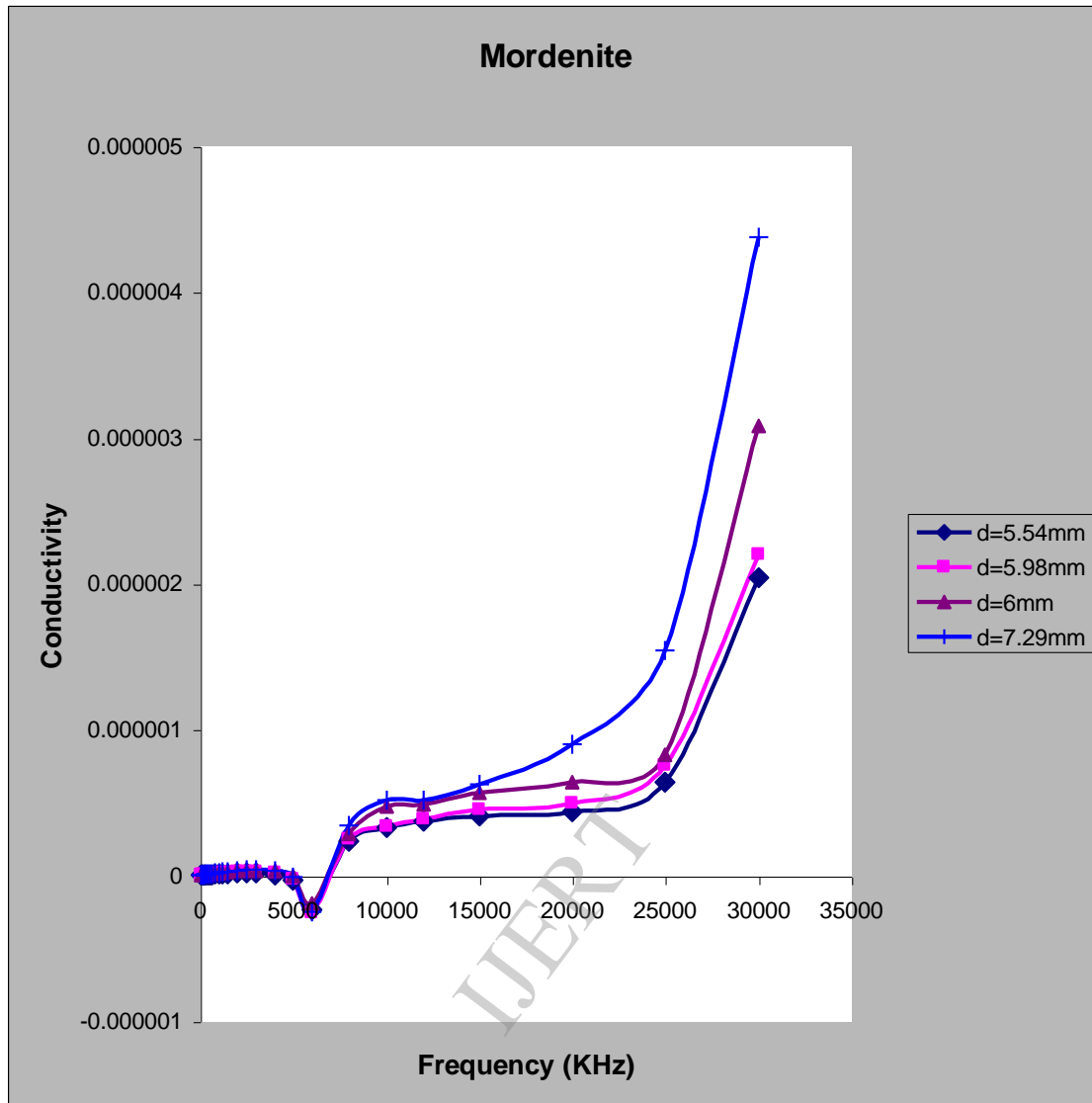
Fig. 1.8 variation of condivity as function of frequency
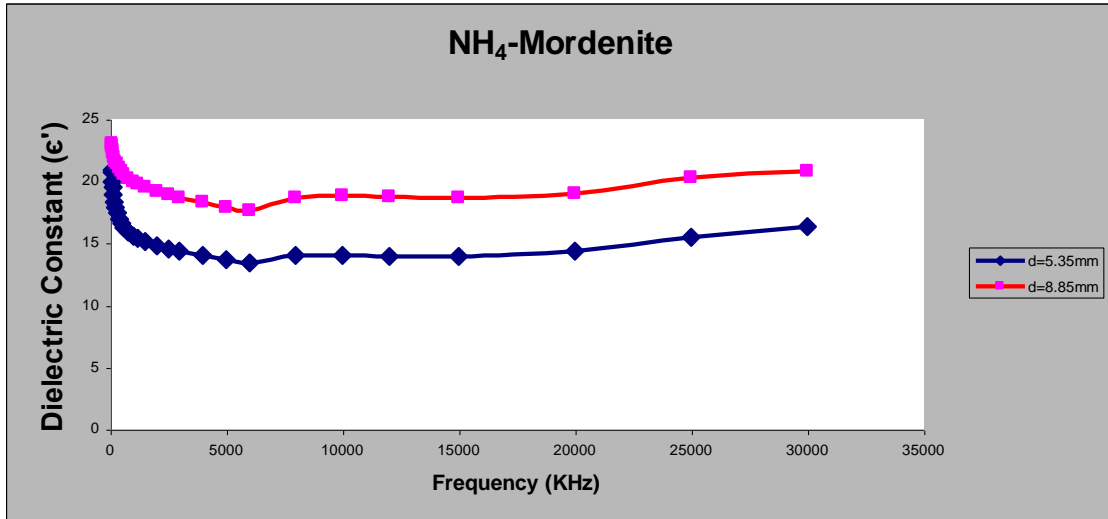
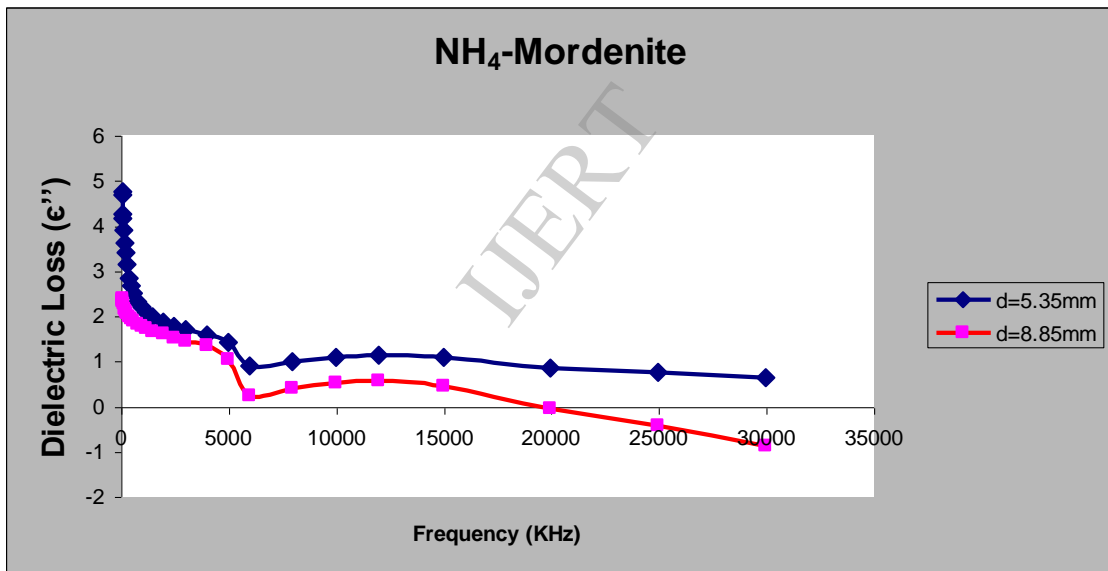*Fig.1.9 variation of dielectric constant in NH₄ mordnite as a frequency*

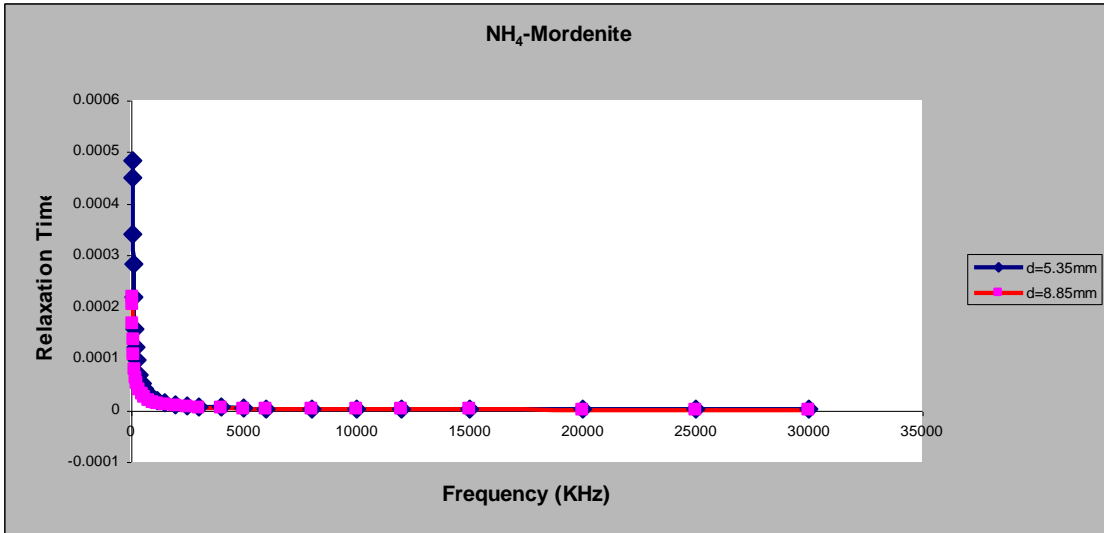*Fig.1.10 Variation of dielectric loss as frequency in NH₄ mordnite*

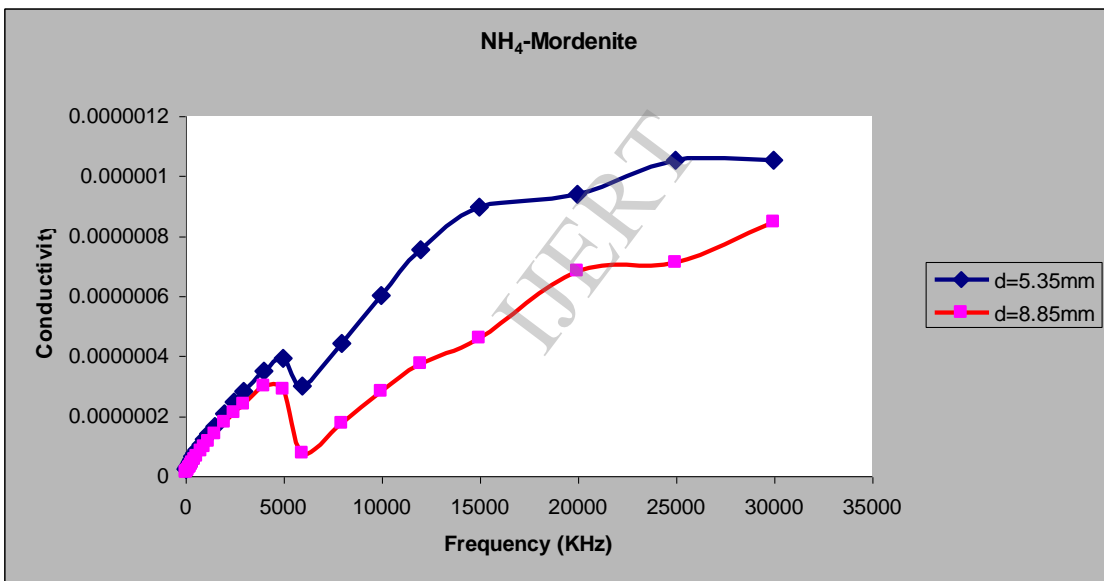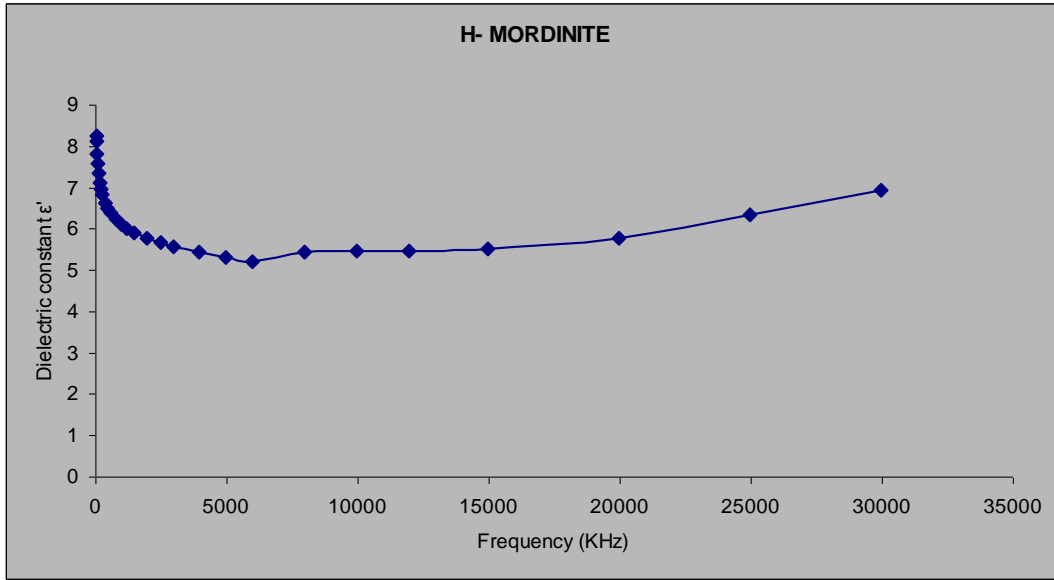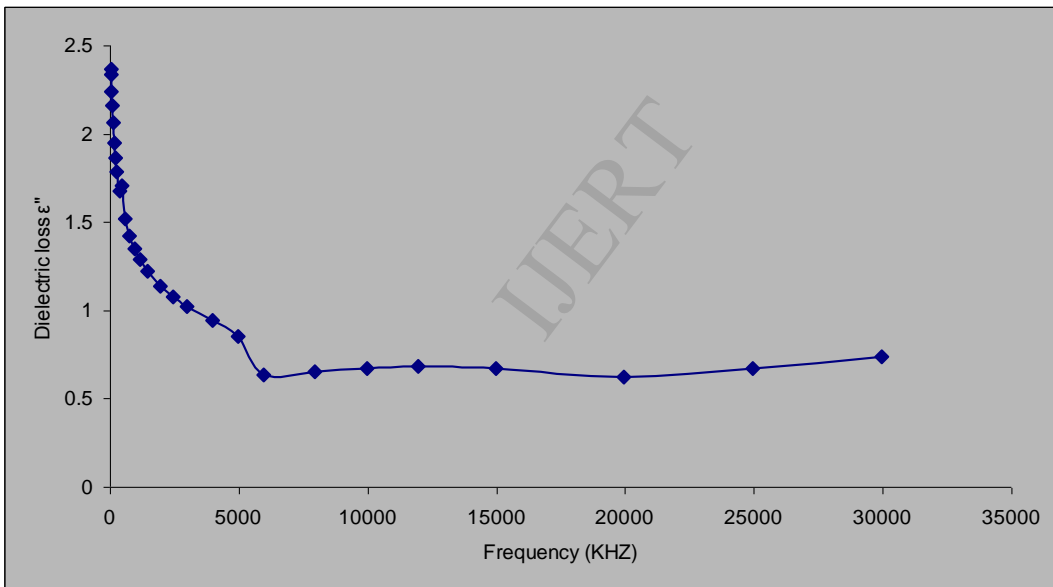*Fig. 1.11 Variation of relaxation time as a frequency in NH$_4$ mordnite*

Fig. 1.12variation of condivity as frequency in NH$_4$ mordnite

Fig.1.13

Variation of dielectric constant as frequency in H mordnite

Fig. 1.14 *Variation of dielectric loss as frequency in H mordnite*

H- Mordenite
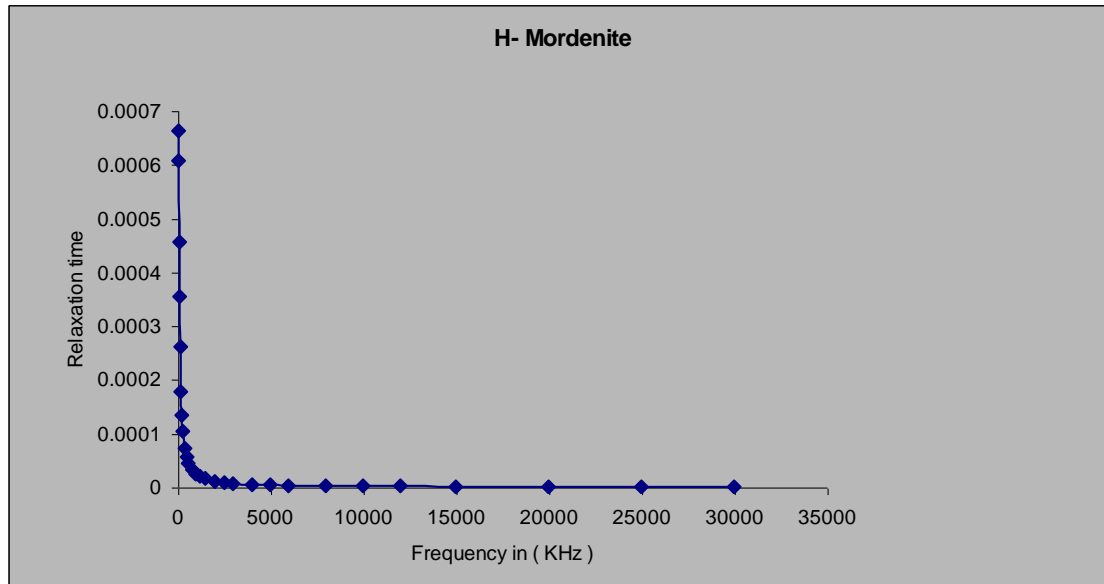
Fig.

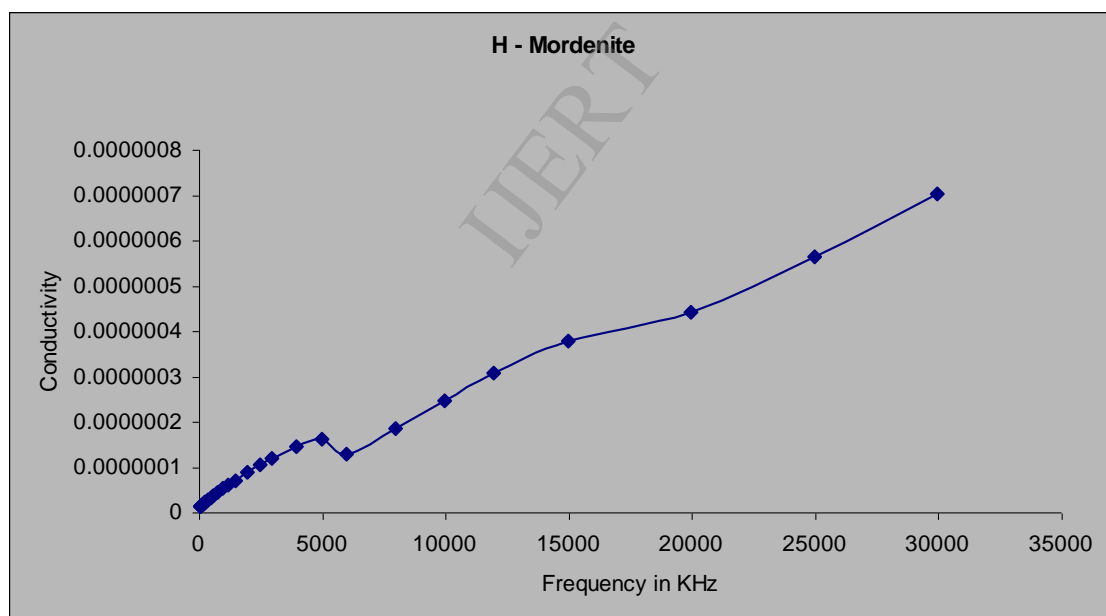*1.15 Variation of relaxation time as frequency in H mordnite*

H - Mordenite

Fig.3.16 Variation of conducitivity as frequency in H mordnite

3) **Relaxation Time (τ)** :- Fig. 3.11 shows the frequency verses Relaxation time τ of NH$_4$ Mordenite goes on decreasing with increase in frequency.

4) **A.C. Conductivity** :- Fig 3.12 shows the variation of A.C. Conductivity against the frequency A.C. Conductivity increases with increase in frequency. Conductivity goes on increasing up to 5000 KHz. It decrease up to 6000 KHz and

again increase linearly up to 30 MHz. As the frequency increases relaxation time goes on decreasing, which increases the A.C. conductivity.

H – Form Mordenite

1) **Dielectric constant Є':-**Fig shows 3.13 the variation in dielectric constant against frequency. The dielectric constant goes on decreasing in H – form Mordenite up to 6000 KHz. Then increases slowly or remain constant.

2) **Dielectric Loss (Є'')**Fig 3.14 shows the variation in dielectric loss against frequency in H-form of Mordenite. Dispersion in dielectric loss is due to the space charge polarization a peak in ε" also occurs at one frequency since the most energy is dissipated at that point This shows that Dielectric loss decreases with increase in frequency decrease in loss up to 600 KHz is rapid then it remain constant up to 30 MHz.

3) **Relaxation Time (т)**:- Fig 3.15 shows the frequency verses Relaxation Time, this shows that **т** goes on decreasing with increase in frequency.

4) **A.C. Conductivity**:- Fig 3.16 shows the variation in A.C. Conductivity with increase in frequency. The A.C. conductivity goes on increasing with increase in frequency. As the frequency increases relaxation time goes on decreasing, which increases the A.C. conductivity.

7 Conclusions

1] Intensity variation is observed in XRD patterns of as grown Mordenite, NH_4 ion exchange form and H-form. The variation in the intensities may be due to difference in scattering factor of cations.

2]IR bands & XRD of Mordenite do not change with temperature of H – form and NH_4 exchange form. This Confirms the stability of Mordenite.

3]Dielectric study of Mordenite plays an important role in stating the nature of zeolite.

The dielectric constant of zeolite is usally composed of four contributions 1) ionic 2) electronic 3) Orientational and 4) Space charge polarization . All these may be operative at low frequency as well as high frequency. Infact the nature of the variations of Є' and Є'' with frequencies indicates which contributions are present. It is observed that the large values of the dielectric constant at the low frequencies exhibited at room temperature may be

attributed to space charge polarization.(8).The space charge contribution will usually depend on the purity and perfections of crystal.

Є' of the dispersive media decreases because of the term contribution to dielectric constant from the ion dipole interaction leading to relaxation of the polarization (9)

Acknowledgements

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