

## Dielectric Study of Mesopores Material Stilbite

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**Abstract:-** Zeolite Stilbite 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:-** Stilbite, Characterization,Dielectric study

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### I. INTRODUCTION

In any solid porous body, various pores can be differentiated depending upon their sizes: micropores, mesopores (Transitional pores) and macropores (1). The micropores are smallest, average radii being less than  $15 - 16 \text{ \AA}$ . Pores with radius less than  $15 \text{ \AA}$  but not less than  $5 - 7 \text{ \AA}$  are called supermicropores.

In mesopores, the effective radii are from  $15 \text{ \AA}$  to  $2000 \text{ \AA}$ . The intensity of the adsorption interaction is less than that in micropores (2). Macropores are characterized by the radii greater than  $2000 \text{ \AA}$ . Micro and mesopores are responsible for adsorption.

Natural zeolites are characterized by micro porosity. The micro porosity results from the specific crystalline structure of the zeolite particles which in turn depends upon its composition. Existence of apertures of fixed diameters causes the molecular sieving action of zeolites. Under ideal conditions some molecules can pass through the apertures to the internal structure filling the available adsorptive space. Others (of larger size) cannot enter and remain on the outer surface of the zeolites grain. Zeolite is an alkaline hydrated aluminosilicate with a skeletal structure (3) containing voids occupied by ions and molecules of the water having a considerable freedom of movement that leads to ion exchange and reversible dehydration.

Stilbite is a natural zeolite belonging to the Heulandite group with unit cell formula  $\text{Ca}_4[(\text{AlO}_2)_8(\text{SiO}_2)_{28}]28\text{H}_2\text{O}(4)$ . The zeolite framework can be described as a fundamental polyhedral configuration containing four and five member rings of tetrahedra. Two sets of interconnected channels exist in the Stilbite structure. A larger 10-member ring channel with  $4.91 \text{ \AA} \times 6.2 \text{ \AA}$  window size in the [100] direction and a smaller eight ring channel with the size of  $2.7 \text{ \AA} \times 5.6 \text{ \AA}$  in the [101] direction (5). The inner surface should therefore be readily accessible to the small molecules. Stilbite is a monoclinic zeolite. The unit cell constants are  $a = 13.61 \text{ \AA}$ ,  $b = 18.24 \text{ \AA}$ ,  $c = 11.27 \text{ \AA}$ ,  $\beta = 127^\circ 54'$ . Stilbite zeolite could potentially be used as an adsorbent and catalyst. It is generally believed that collapse of the Stilbite structure during dehydration is due to the presence of exchangeable cations [6]. When removing the water molecule legends, the cations must coordinate directly to the oxygen in the framework. Because of their high charge density, the cations can distort the framework to achieve the best environment for possible coordination. The distortion in Stilbite is so serious that some of the bonds connected to tetrahedral atoms (Silicon or aluminum) break, rendering the zeolite almost useless as an industrial catalyst or dehydrating agent (7).

Since destruction of the Stilbite framework is closely related to the exchangeable cations it might be possible to stabilize the framework by reducing the number of exchangeable cations. Beyer et al (8) performed a thermogravimetric study of the de ammoniation of  $\text{NH}_4$  - Stilbite in oxidizing and inert atmosphere and reported the structure variation of the H-Stilbite thus formed. Mortier and coworkers (9) investigate the crystal structure of  $\text{NH}_4$  - Stilbite dehydrated at  $300^\circ\text{C}$ , and found only a minor distortion with respect to the hydrated form. The framework remains open and the residual cations are located in eight rings. In the case of Stilbite, the hydrogen form is more stable (10,11). The framework of  $\text{NH}_4$  - Stilbite heated in a shallow bed reactor remains up to the temperature of  $500^\circ\text{C}$ . The thermal stability of the zeolite increases with increasing degree of ammonium exchange. The thermal behaviour of Stilbite is studied recently (12). The collapse of the framework can be prevented by reduction of the cation / framework interaction.

### II. SAMPLE PREPERATION

Stilbite were collected from the quarries of Ajanta caves. Sample crushed and sieved to get  $106 \mu\text{m}$  sized crystals for  $\text{NH}_4$  - ion exchanged form of STI, sample is treated with 1 M solution of  $\text{NH}_4\text{NO}_3$  with stirring at  $95^\circ\text{C}$  for six hours. To form H-form Stilbite,  $\text{NH}_4$ - STI heated at  $250^\circ\text{C}$ .

### III. CHARACTERIZATION

**X-ray diffraction-** For the characterization of Stilbite, X-ray diffractograms were recorded between  $2\theta$  values from  $5^\circ$  to  $50^\circ$  on Phillips (PW 1710) having the wavelength  $1.94056 \text{ \AA}$ . Diffractograms of three forms of Stilbite are recorded.

#### IR

The IR spectra of Stilbite were recorded on Perkin – Elmer . 221 spectrophotometer in the frequency range  $400$  to  $4000 \text{ cm}^{-1}$ , of parent form,  $\text{NH}_4$  – form, Parent at  $100^\circ\text{C}$ , Parent form at  $150^\circ\text{C}$ , Parent form  $200^\circ\text{C}$  & H – Form of Stilbite.

The observed IR bands and assignment are given in table 2

### IV. CHEMICAL FORMULA OF STILBITE

The chemical formula of Stilbite is as follows

- 1) **Parent Stilbite**  
 $\text{Na}_{0.5} \text{K}_{0.07} \text{Ca}_{3.37} [\text{Si}_{24.36} \text{Al}_{7.30} \text{O}_{72}] 31 \text{H}_2\text{O}$
- 2) **H – form Stilbite**  
 $\text{H}_{2.94} \text{Ca}_{1.0} [\text{Si}_{24.36} \text{Al}_{7.30} \text{O}_{72}] 31 \text{H}_2\text{O}$

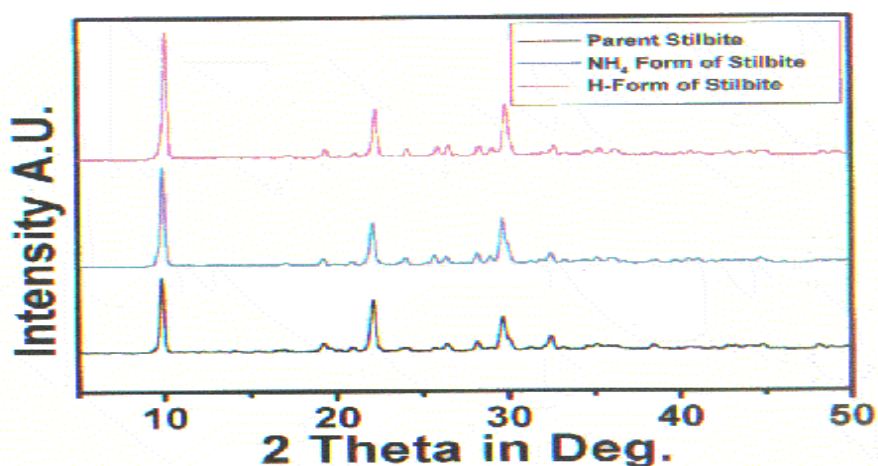


Fig. 1 XRD pattern of stilbite

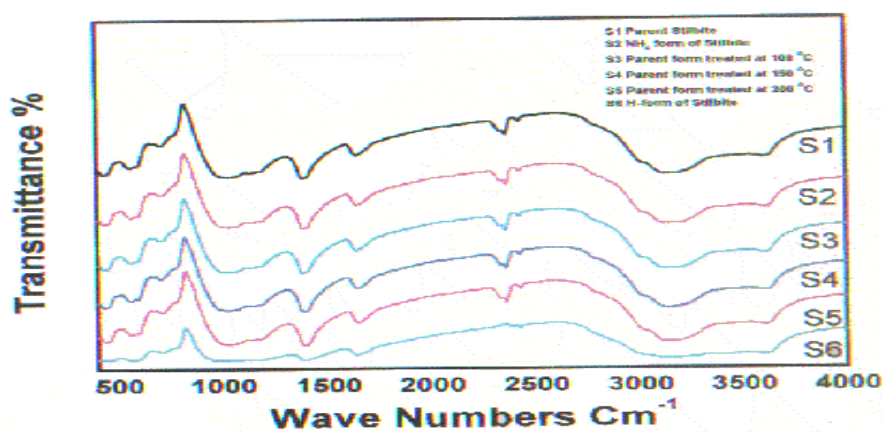


Fig. 3 IR OF Stilbite from 400- 4000

## V. RESULT AND DISCUSSION

**XRD** – XRD Pattern of parent Stilbite, NH<sub>4</sub> – form of Stilbite & H – form of Stilbite is shown in fig.1 from diffractogram. There are no major changes in these three forms which confirm the stability of Stilbite. ‘d’ values are compared with standard ‘d’ values.

**IR** – From IR studies structure sensitive Asymmetric stretch is at 1417 cm<sup>-1</sup> and symmetric stretch is at 833 cm<sup>-1</sup>. Water bands of hydroxy stretch is at 3605 cm<sup>-1</sup> & water bands at 1659 cm<sup>-1</sup>. Internal tetrahedral symmetric stretch is at 443 cm<sup>-1</sup>. Asymmetric stretch is at 1045 cm<sup>-1</sup>. Assignment for T-O bending is at 443 cm<sup>-1</sup>. The nature of IR bands is same for parent form, NH<sub>4</sub> – form & H – form which confirms the stability of Stilbite.

Sample Name	External linkage cm <sup>-1</sup> Str. sensitive		Double ring	Internal Tetrahedral Str Insensitive cm <sup>-1</sup>		T – O Bend	Water Bands	
	Asymmetric Stretch	Symmetric stretch		Asymmetric Stretch	Symmetric stretch		OH-stretch	H <sub>2</sub> O Bands
Stilbite	1417	833	616	1045	816	443	3605	1659

Table.2 IR assignments in Cm<sup>-1</sup>

## VI. DIELECTRIC STUDIES OF STILBITE DIELECTRIC CONSTANT :

The relative permittivity,  $\epsilon$  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

$\epsilon_0$  = 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  $\delta$  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  $\epsilon^*$  is the complex relative permittivity

$\epsilon''$  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<sup>-12</sup> to 10<sup>-10</sup> 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  $\alpha$  and other is  $\beta$ .  $\alpha$  relaxation occurs at low frequency due to micro brownian motion within chain

$\beta$  Relaxation occurs at higher frequency due to dipole orientation as well as torsional movement of chains

$$\text{Reax time } T = \epsilon'' / \omega \epsilon'$$

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

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

2 Theta	d-Value	Peak Width	Intensity
09.75	9.08	0.10	100
16.78	5.29	0.24	2.7
19.09	4.65	0.24	11
20.76	4.28	0.12	6.3
21.91	4.06	0.18	56
22.24	4.00	0.12	5.4
23.87	3.73	0.24	4.6
26.25	3.40	0.20	6
28.00	3.19	0.08	11
28.76	3.10	0.24	2.7
29.43	3.04	0.12	25.
29.51	3.03	0.10	32.6
29.81	3.00	0.16	10.6
31.09	2.88	0.24	2
32.25	2.78	0.08	13.5
32.91	2.72	0.12	2.5
35.04	2.56	0.20	4.6
38.36	2.35	0.24	3.6
40.55	2.22	0.16	2
42.57	2.12	0.24	1.7
43.83	2.06	0.32	2.5
44.66	2.03	0.24	3.9
47.90	1.90	0.32	1.4

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

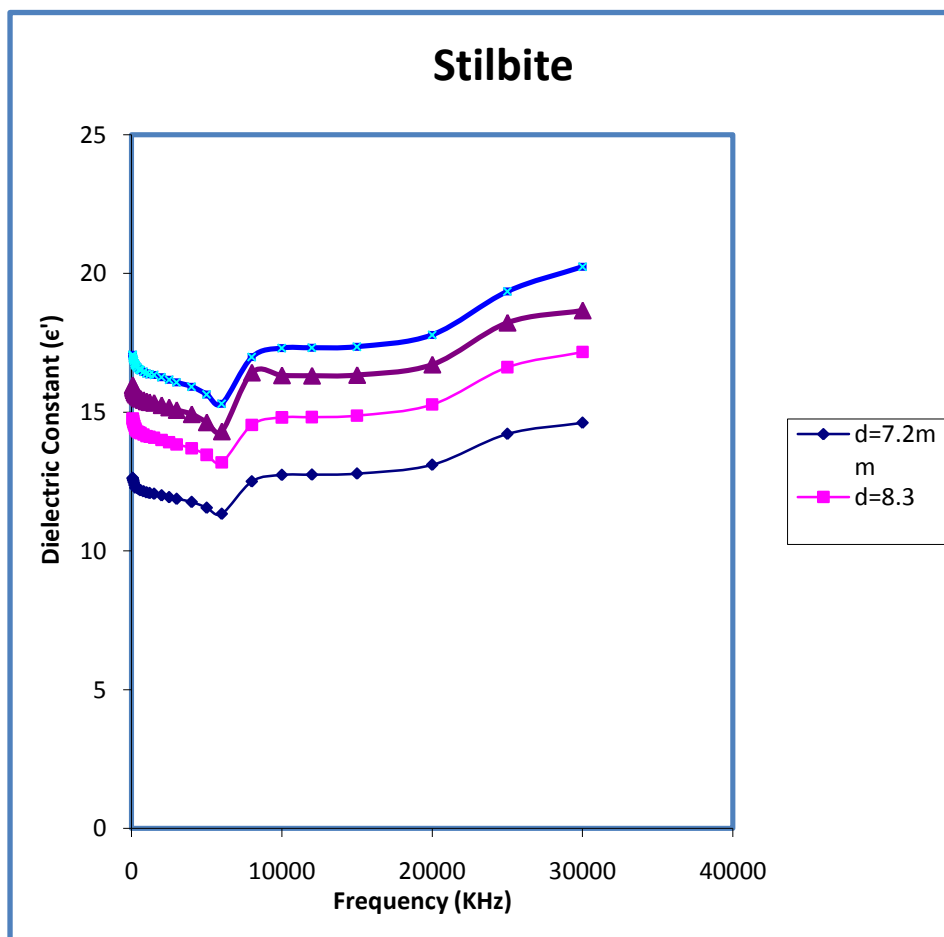


Fig. 5 variation of dielectric constant as a frequency in stilbite

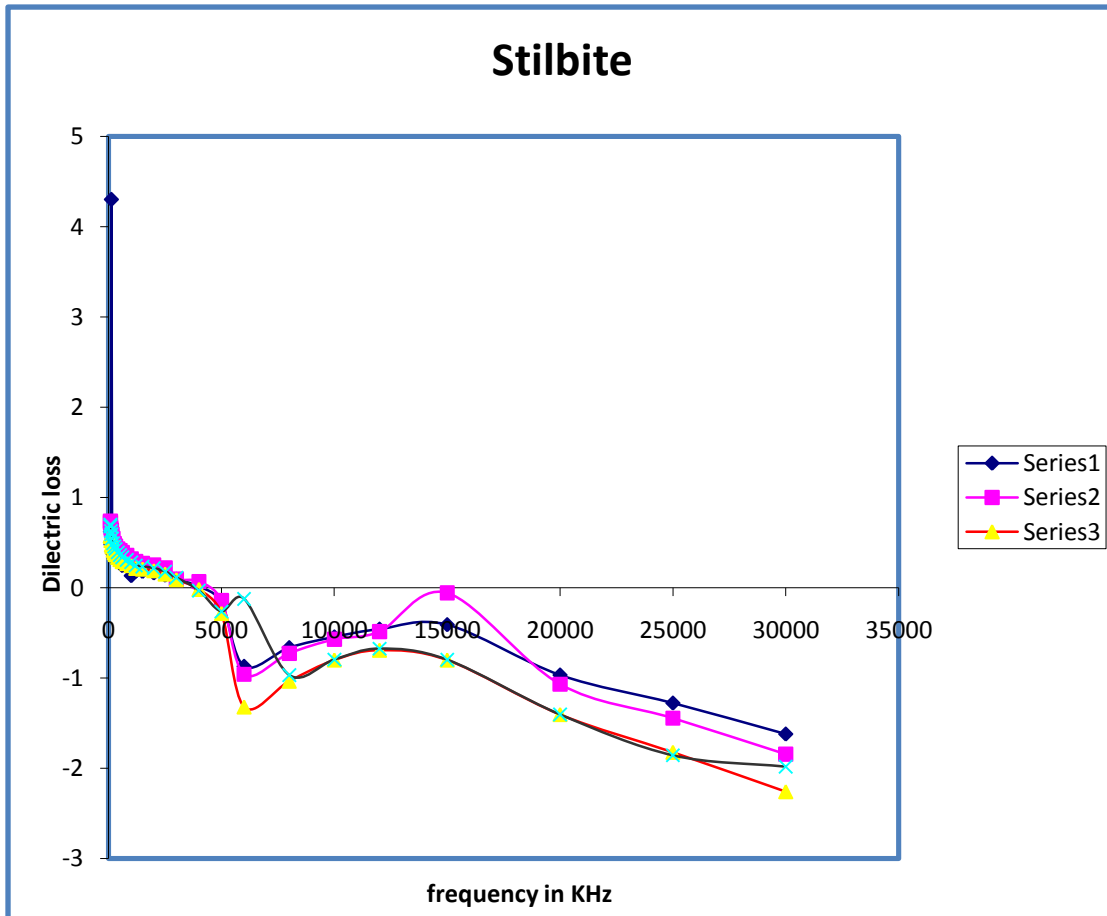


Fig. 6 variation of dielectric loss as a frequency in stilbite

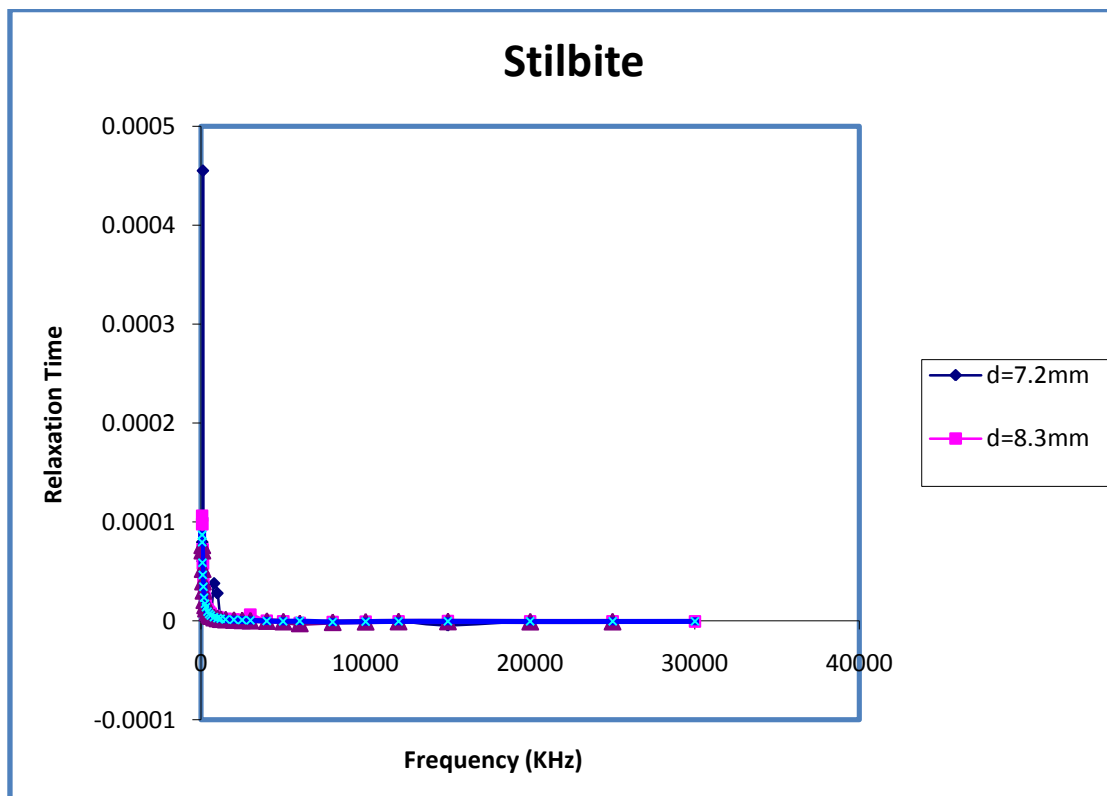


Fig. 7 variation of relaxation time as a frequency in stilbi

## VII. CONCLUSIONS

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

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