Materials Science Research India Volume **3**(1a), 109-113 (2006)

STUDIES ON STRUCTURAL PROPERTIES OF HEULANDITE CRYSTALS FROM MARATHWADA, INDIA

S.D. Ghan*, H.V. Bakshi[a], M.W. Kasture[b] and B.T. Bhoskar

*Department of Physics & Electronics, Yogeshwari Mahavidyala, Ambajogai, District Beed (India)
[a]ACS College, Shankarnagar, Tq. Biloli, District Nanded (India)
[b] National Chemical Laboratory, Pune (India)
[c] Nutan Mahavidyala, Sailu, District Parbhani (India)

(Received: May 15, 2006; Accepted: June 02, 2006)

ABSTRACT

Eight different type of heulandite crystals were collected from Marathwada region of India. These were characterized by x-ray diffraction (XRD), thermogravimeterc analysis (TG) and infrared spectroscopy (IR). The intensities of the peaks of XRD's have been compared. The weigth loss due to desertion of water has been estimated by therogravimetric analysis. The framework structure of these heulandite crystals were studied by infrared spectroscopy.

Key words: heulandite; X-ray diffraction; Thermogravimetric analysis; Infrared spectroscopy; Framework structure.

INTRODUCTION

The framework structure of zeolites consists of intracrystalline channel and voids. The cation usually present in the nature zeolites are Ca, Na and K, this extra framework cation are loosely bound to the framework. The number of zeolites minerals tectosilicates and clay minerals have been studied by

Infrared spectroscopy

A systematic investigation of the framework structure of zeolites was carried out by flanigen et.al.[1]. The infrared structure analysis of some natural and synthetic zeolites was also reported[2-4]. The interpretation of the spectra were based on assignment of the infrared (IR) bands to certain structure groups in various zeolites frameworks. On the basic of framework topology and identical elements of secondary building units, zeolites have been classified in seven groups. According to this, heulandite comes under VII group of platy zeolites[5]. Heulandite is a common natural zeolite having the chemical composition $(Ca, Na)_2 Al_2Si_7O_{18}.16H_2O$. The structure of heulandite has been studied by many workers[6,7].

In the present investigation, a few varieties of natural heulandite crystals from different localities of Marathwada region of India were collected and characterized by X-ray diffraction, thermogravimetric analysis and infrared spectroscopy. An attempt has been made to compare the structure of heulandites collected from different localities.

EXPERIMENTAL

The samples were collected from different localities of Marathwada region of Maharashtra, India. The collected crystals were found to be platy in nature and greenish, orange, grey, pearl white in colours.

The crystals were separated from the rock samples, then cleaned, crushed and sieved to get

150 µm sized crystals. Powdered samples were washed with distilled water and dried in an oven at 100°C for the period of 12 hours. The samples were designated as H-1 to H-8.

These samples were characterized by different instrumental techniques to study their structural properties. The techniques used are X-ray diffraction, infrared spectroscopy and thermogravimetric analysis.

X-ray diffraction

The X-ray diffractograms of the samples were recorded by using Phillips Diffractrometer, Nickel Filter, CuKa radiation (l = 1.5406 A°) with the chart speed of 4°C/min, in the 2t values ranging from 5°-40°. The 'd' values calculated were found to be in good agreement with the standard ASTM data. The diffractrometer are shown in Fig. 1.

Thermogravimetric analysis

The thermogravimetric analysis of the samples were carried out on 'Seiko Thermoanalyser, Japan' at the heating rate of 10°C/min. from 30° - 480°C and are shown in Fig. 2.

Infrared studies

The infrared spectra of the samples were recorded on 'Shimadzu C' infrared spectrophotometer using KBr wafer technique in the range 400-4000 cm^{-1}. These spectra are shown in Fig. 3.

RESULTS AND DISCUSSION

Fig. 1 depicts the XRD patterns for the samples H1 to H8 recorded at room temperature (30°C). The XRD patterns of all the samples are in good agreement with the data published for

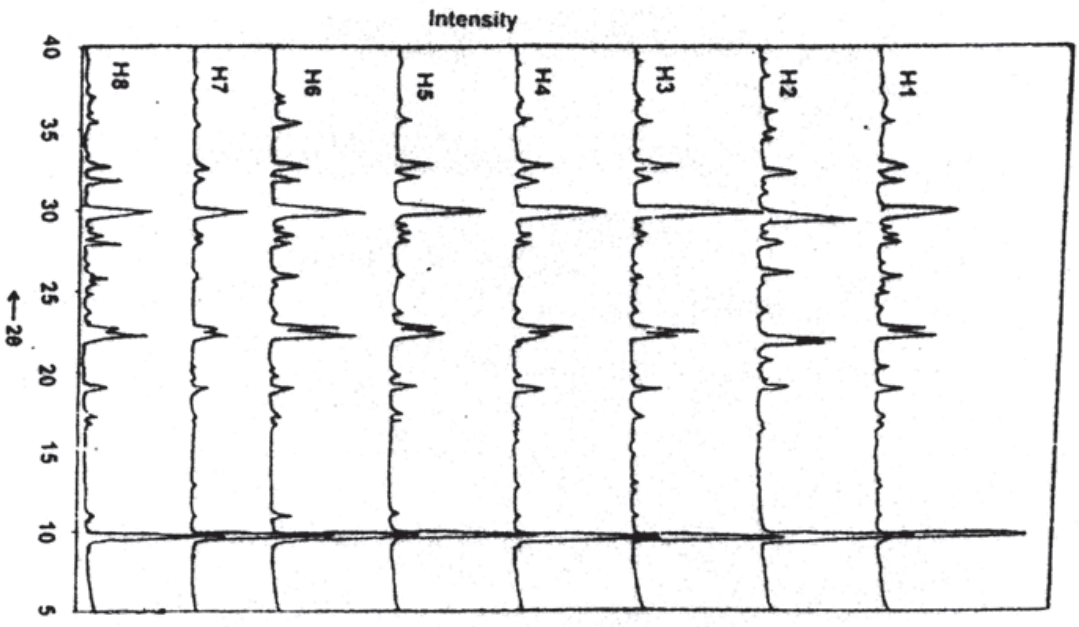

Fig. -1: X-ray diffractograms of heulandites

heulandite. The XRD pattern reveals the crystalline nature and phase purity of all the samples. The XRD also establishes the absence of amorphous material in the zeolite samples. It has been cleared from the Fig. 1 that the XRD patterns of all the samples are identical but differ in the intensities of the peaks. This variation may be due to the difference in scattering factor of cations which are incorporated in the structure[8].

Thermogravimetric analysis

Zeolites are classified into two groups on

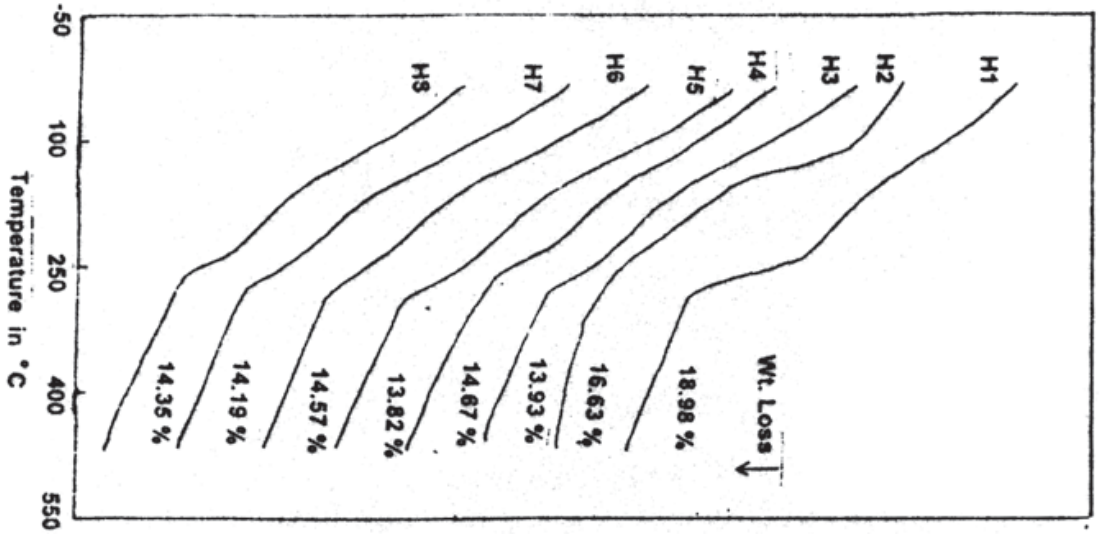

Fig. - 2: TG Curves of heulandites

the basis of their dehydration behaviour as follows:

1) Those which show no major structural changes during dehydration and which exhibits continuous weight loss as a function of temperature.
2) Those which undergo major structural changes during dehydration and exhibits discontinuities in their weight loss curve.

Heulandite belongs to group second of zeolites and it has been reported that the structure of heulandite changes from heulandite A to heulandite B after the thermal treatment at 230°C ± 10°C. Fig. -3 shows the TG curves of the samples recorded from 30°C to 480°C. It is observed that the weight loss during the thermal treatment is in steps. From Fig. 3, it is clear that though the collected zeolite samples are of heulandites, their weight loss due to desorption of water is different. It may be due to the difference in extra framework cations.

Table - 1: Infrared spectral data of Natural Heulandite Samples

Sample Name	Internal Tetrahedra (cm^{-1})			External linkages (cm^{-1})		Pore Opening	Water Bands	
	Asymmetric Stretch	Symmetric Stretch	T-O bend	Asymmetric Stretch	Symmetric	Stretch	H_2O Bend	O-H Stretch
H1	1020	670	443	1140	770	405	1631	3396
H2	1020	670	436	1150	760	-	1631	3360
H3	1018	670	434	1130	760	-	1630	3360
H4	1020	670	440	1140	760	420	1630	3360
H5	1022	670	424	1160	760	-	1635	3402
H6	1047	670	455	1180	760	420	1630	3396
H7	1045	670	443	1200	760	405	1630	3392
H8	1045	670	445	1150	770	420	1630	3392

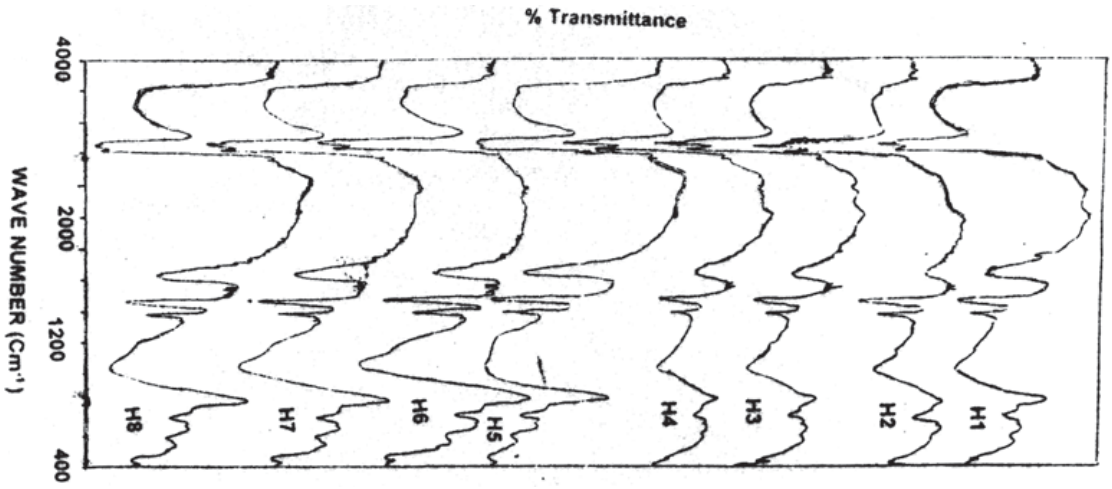

Fig. - 3: Infrared spectra of heulandites

Infrared studies

Infrared spectral studies provide information about the polyhedral framework structure and composition of a zeolite structure. Such a study can be used to find a systematic change in the framework structure and composition by various treatments of the zeolites samples. Zadanov *et al.*[9,10] used infrared spectroscopy to study the major structural changes and the Si/Al variation in the framework during the dehydration. However, in the present study we have compared the IR spectra of the heulandite samples collected from different localities, located far away from each other, at room temperature. Fig. 3 shows the IR spectras of the samples. The observed spectral frequencies of the zeolites under study are given in Table 1. In general these spectra cover the range 400-4000 cm^{-1} rather than the bands which are attributed to water, other absorption bands are related to framework structure. It is observed that every zeolite appears to exhibit a typical infrared pattern. The spectra are divided into two groups:

1) Those due to internal vibrations of TO_4 tetrahedron which is the primary building units of the structure. These vibrations are not sensitive to other structural variations.
2) Those due to vibrations which may be related to the linkages between tetrahedral. These vibrations are sensitive to the overall structure and to the joining of the individual tetrahedral in secondary structure units as well as their existence in the larger pore-opening.

The first class of spectra consists of strong absorption in the range 950-1250 cm^{-1} which is assigned to internal asymmetric stretch. It can be seen from the Table-1, that these values are ranging between 1010-1047 cm^{-1}. There is another asymmetric stretching mode, corresponds to weak absorption at 1160 cm^{-1} which is sensitive to structural changes. A strong band in the region 500-420 cm^{-1} is assigned to T-O bending mode. However, absorption band in the region 650-750 cm^{-1} are found to be weak and attribute to internal and external asymmetric stretches. The internal symmetric mode has been observed a weak absorption at 670 cm^{-1} and another weak absorption at 760 cm^{-1} corresponds to external symmetric stretch and which is structural insensitive.

The second group of frequencies appear in the region 500-650 cm^{-1} and 300-420 cm^{-1}. These are due to the linkage between tetrahedral and mode of arrangements of the secondary building units of the zeolite structure.

Association of water molecules with the cations and framework oxygen of a zeolite depends upon the openness of the structure[12,13]. In the zeolite study the absorption due to water molecules appear as a strong broad band around 3360 cm^{-1}. The

bending mode at 1630 cm^{-1} has also been observed.

Conclusion

The colour of the crystals may be due to accessory elements in the structure of the zeolite. This presence of accessory elements in the structure of respective healandite gets exhibited through its changed XRD and IR pattern. From the IR study, is inferred that the exchange in frequencies in the region of 1150-1050 cm^{-1} (Ext. asym. Stretch) and 450-420 cm^{-1} (T-O bend) varies with the colour of the crystals in this case of investigation. While other absorption bands doesn't show any appreciable change in their frequencies. The XRD patterns reveal the impurities in their structural sites and thermogravimetric analysis supports the change in the extra framework cations of the structure.

REFERENCES

1. Flanigen, E.M., Khatami, H. and Szymanski, H.A., Molecular Sieve Zeolites – Advances in Chemistry series 101, *Am. Chem. Soc.,* Washington D.C. 201 (1971).
2. Joshi, M.S. and Bhoskar, B.T., *Ind. J. Pure and App. Phys.,* **19:** 560 (1981).
3. Joshi, M.S., Joshi, V.V., Choudhari, A.L. and Kasture, M.W., *Mat. Chem. & Phys.,* **48:** 160 (1997).
4. Bhoskar, B.T. and Ghan, S.D., *Asian J. Chem.,* **14**(1): 427 (2002).
5. Gottardi, G. and Galli, E., *Natural Zeolites,* Springer Berlin, 256 (1985).
6. Kasture, M.W., Tamhankar, S.S., Joshi, V.V., Choudhari, A.L. and Shiralkar, V.P. *J. Adsorp. Sci. and Technol.,* **15:** 717 (1997).
7. Ghan, S.D. *Ph.D. Thesis,* S.R.T.M. University, Nanded (1999).
8. James, R.W. and Brindley, G.W., *Z. Krist.,* **78:** 470 (1931).
9. Zadanov, S.P., Kiseleve, A.V., Lygin, V.J. and Tilove, T.J., *Zh. Fiz. Khim.,* **38:** 2408 (1964)
10. Zadanov, S.P., Kiselev, A.V., Lygin, V.J. and Tilove, T.J., *Zh. Fiz. Khim.,* **38:** 2408 (1964).
11. Breck, D.W., Zeolite Molecular Sieves, John Wiley, New York. 418 (1974).
12. Bertsch, L. and Habgood, H.W., *J. Phys. Chem.,* **67:** 1621 (1963).
13. Angell, C.L. and Schagger, P.C., *J. Phys. Chem.,* **69:** 3463 (1965).