

Dehydration of natural stilbite: An in situ FTIR study

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ABSTRACT

The dehydration behavior of a natural stilbite sample from Poona (India) was investigated by in situ FTIR. The thermal induced variations of the water molecule bending (ν_2) mode around 1653 cm^{-1} , the stretching (ν_3 and ν_1) modes around 3587 and 3426 cm^{-1} , and the corresponding second-order modes in the wavenumber region $4000\text{--}8000\text{ cm}^{-1}$ were followed as indicative of the dehydration process. The observed spectral variations indicate that stilbite undergoes a transformation at about 448 K due to the loss of half of the original content of water molecules. The rehydration of stilbite is partial in samples heated up to 630 K . Concerning both the dehydration and rehydration behaviors of stilbite, our results are in concert with those proposed in the literature. In addition, the growth of a new mode around 4550 cm^{-1} is observed in the temperature range $430\text{--}650\text{ K}$ and may indicate the presence of hydroxyl groups created by the breaking of the T-O-T linkages.

INTRODUCTION

Stilbite, $(\text{Na}_2\text{Ca}_8)[\text{Al}_{18}\text{Si}_{54}\text{O}_{144}]\cdot 60\text{H}_2\text{O}$, is a common zeolite with framework type [STI] and topological symmetry of the framework orthorhombic, $Fmmm$. The real symmetry is $C2/m$ with no Si/Al-order in the framework (Galli 1971; Slaughter 1970). However, the symmetry of stilbite is often referred as $F2/m$ to facilitate its comparison with other related structures (Cruciani et al. 1997). The framework is composed of ten- and eight-membered rings and the zeolite cavities are occupied by Ca and Na and coordinated water molecules (Slaughter 1970). Stilbite shares the same framework type [STI] with stellerite, $\text{Ca}_8[\text{Al}_{16}\text{Si}_{56}\text{O}_{144}]\cdot 56\text{H}_2\text{O}$, and barrerite, $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{56}\text{O}_{144}]\cdot 52\text{H}_2\text{O}$. Stellerite (Galli and Alberti 1975a; Miller and Taylor 1985) has the same framework as stilbite, no Si/Al-order in the framework, and a higher symmetry $Fmmm$ ($Z = 2$), which coincides with the topological symmetry of the framework. The symmetry of barrerite is orthorhombic $Amma$ ($Z = 2$) (Galli and Alberti 1975b) with a shift of one extraframework position, which causes the framework to rotate around a screw diad parallel to **a**. Again, no Si/Al-order is observed in the framework.

Water is an essential constituent of zeolites and low temperature ($<400\text{ }^\circ\text{C}$) dehydration and rehydration processes of the “zeolitic water” is an important property utilized in various industrial applications. An essential aspect of dehydration is the concomitant formation of various defects, a partially irreversible process that may modify the physical-chemical properties of zeolites. For example, we know that cyclic dehydration of zeolites accumulate acid sites (chemical defects) on the internal surface of the crystal (Moroz et al. 2003). The number of these defects, accumulated during several dehydration-rehydration cycles, is too small to change the crystallographic or absorption properties of zeolites. However, it is sufficient to induce a remarkable enhancement of the rate of proton transfer reaction

in the cavities and consequently to modify the properties closely related to the active sites, such as catalytic activity and proton conductivity (Moroz et al. 2003).

The structure of stilbite and its dehydration and rehydration properties make it a potential adsorbent and catalyst. However, collapse of the framework during dehydration is a disadvantage because the ability to rehydrate at lower temperatures could be effectively used in ion exchange processes (Mortier 1983). Thus, it is important to investigate the thermal behavior of this zeolite and its structural stability region.

The thermal transformations of stilbite have been studied by various experimental methods such as thermal analysis and X-ray diffraction (XRD). The thermo-gravimetry (TG) and differential thermal analysis (DTA) investigations reported by Gottardi and Galli (1985) show two endothermic peaks at about 448 and 523 K . These peaks were interpreted as the progressive loss of about 30 and 26 water molecules, respectively. The residual water molecules were lost at higher temperature. The dehydration and rehydration processes of stilbite were also investigated by Aumento (1966) who showed that samples heated below 573 K were completely rehydrated whereas samples heated to $573\text{--}873\text{ K}$ were only partially rehydrated. Rykl and Pechar (1985) also reported that stilbite transforms into meta-stilbite at about 533 K and into an amorphous phase above 743 K . Joshi et al. (1982) and Kasture et al. (1997) also reported on stilbite and its thermal products from the Deccan trap region using XRD, DTA-TG, and IR spectroscopy. Cruciani et al. (1997) studied the dehydration processes of stilbite using in situ synchrotron X-ray powder diffraction. They reported a stepwise dehydration mechanism and a change in the crystal symmetry (stilbite B, orthorhombic-*Amma*) at about 420 K . In the higher temperature range, i.e., in the stilbite B phase, a continuous dehydration and breakage of T-O-T ($T = \text{Si or Al}$) bonding was observed. The decomposition of stilbite is accomplished above 720 K .

If we consider the thermal behavior, zeolites may be classified into the following categories (Bish and Carey 2001): (1)

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reversible dehydration with little or no modifications in the framework and cell volume; (2) reversible dehydration accompanied by large distortions in the framework and a significant decrease in the cell volume; (3) partially irreversible dehydration accompanied by the breakage of T-O-T bonds. The first dehydration step is reported to be reversible, while the second is partially irreversible (Gottardi and Galli 1985). In concert, Cruciani et al. (1997) reported breakage of T-O-T linkages in the stilbite B phase. Similar observations were reported in the heat-collapsed phases of barrerite by Alberti et al. (1983).

Although a wealth of papers found in the literature deal with the dehydration-rehydration of stilbite, to our knowledge, no in situ infrared spectroscopic studies have been performed so far. Thus, the goal of the present investigation is twofold: to probe the thermal behavior of infrared-active fundamental modes of water molecules to understand the dehydration and rehydration processes and to investigate the molecular linkages induced by dehydration using the thermal variations of second order modes in the wavenumber region 4000–8000 cm^{-1} .

MATERIALS AND METHODS

The investigated samples are natural stilbites from the Poona region, India. These samples were used without further purification. Suitable samples were cut from a larger crystal for the NIR studies, whereas powdered samples were used for the other investigations. An electron microprobe (JOEL JXA-8600MX) was used for chemical analysis. For quantification the synthetic and natural standards supplied by the manufacturers were used. The experimental conditions were: diameter of the electron beam 30 μm ; current 20 nA on Faraday cup; accelerating voltage 15 kV.

The X-ray diffraction (XRD) patterns were obtained using a Philips PW-1830 powder diffractometer equipped with a Ni-foil filter and $\text{CuK}\alpha$ radiation. The 2θ scan was from 5–80° 2θ . The sample was rotated at a rate of 3°/min. Powder diffraction patterns were collected from the unheated stilbite sample and its heat-treated products.

Differential scanning calorimetric (DSC) patterns were recorded with a TA Instruments DSC 2010 calorimeter. The weight of the sample was 8 mg and the heating rate was 10 °C/min. The thermo-gravimetric analysis (TG and DTG) was performed using a Mettler Toledo Star TGA/SDTA 851 system. The weight of the powder sample used for the experiment was 37.66 mg. The measurements were performed in the temperature range 300–873 K with a heating rate of 20 K/min.

FTIR studies were carried out with a NEXUS FTIR spectrometer (with sealed and desiccated optics) from Thermo-Nicolet, using a thermo-electrically cooled deuterated triglycine sulfate (DTGS) detector, extended range KBr (XT-KBr) beam splitter, and a dual source working in the wavenumber range 375–12500 cm^{-1} . The samples, 500 μm thick, were placed in a specially manufactured environmental chamber. This chamber can be used to increase the temperature of the sample under study up to about 950 K with an accuracy of ± 2 K. Circulating tap water was used to cool the outer jacket of the chamber, which consists of the infrared transparent windows. The conventional KBr pellet method was used to study the dehydration mechanism of fundamental modes in the wavenumber range 400 to 4000 cm^{-1} , using a NEXUS Ever-Glo source. The spectra were recorded in the wavenumber region 2000 to 8000 cm^{-1} using a white light source (tungsten halogen) and each spectrum is an average of 256 scans with 2 cm^{-1} resolution.

The dehydration behavior of stilbite was investigated in four experiments. In the first experiment the dehydration behavior was probed up to about 775 K, where total dehydration was expected. In the second experiment the maximum temperature was 475 K, which permitted study of both the dehydration and rehydration processes. The third experiment was similar to the second, except that the maximum temperature of the experiment was 630 K. In the fourth experiment we probed the near IR range of the second order modes of water molecules of stilbite to establish that T-O-T bond linkage/breakage induced by the dehydration processes. The maximum temperature at which in situ NIR spectra were taken was 850 K. For all of the experiments we used the bending and stretching modes of water groups and their combination overtone modes to extract information about structural modifications.

RESULTS

The chemical composition determined from the EPMA analysis is $\text{SiO}_2 = 60.17$ (0.757); $\text{Al}_2\text{O}_3 = 16.62$ (0.681); $\text{CaO} = 8.81$ (0.132); and $\text{Na}_2\text{O} = 0.30$ (0.106) wt%. The chemical formula derived from these observations (based on 144 oxygen atoms) is $\text{Na}_{0.52}\text{K}_{0.01}\text{Ca}_{8.52}\text{Al}_{17.69}\text{Si}_{54.32}\text{O}_{144}\cdot 60\text{H}_2\text{O}$. Quartieri and Vezzalini (1987) and Cruciani et al. (1997) also reported some anomalies in the chemical compositions of stilbites, with no appreciable variations in bond distances and framework coordinates.

Powder diffraction patterns collected from the original and heat-treated stilbite samples were compared to the data reported by Galli (1971) and Cruciani et al. (1997) to identify the various phases of stilbite.

The observed XRD pattern for the unheated stilbite sample showed the most intense peaks with d -spacings of 8.99, 6.32, 5.25, 4.62, 4.03, 3.98, 3.71, 3.17, 3.01, 2.98, 2.76, and 2.56 Å, which are comparable to the d -spacings of 8.88, 6.36, 5.23, 4.63, 4.04, 3.99, 3.70, 3.17, 3.02, 2.98, 2.75, and 2.56 Å reported by Galli (1971).

Figure 1a shows a DSC pattern from the natural stilbite sample in the temperature range 300–650 K. A transition/transformation occurs at about 488 K. Another weak transition/transformation is

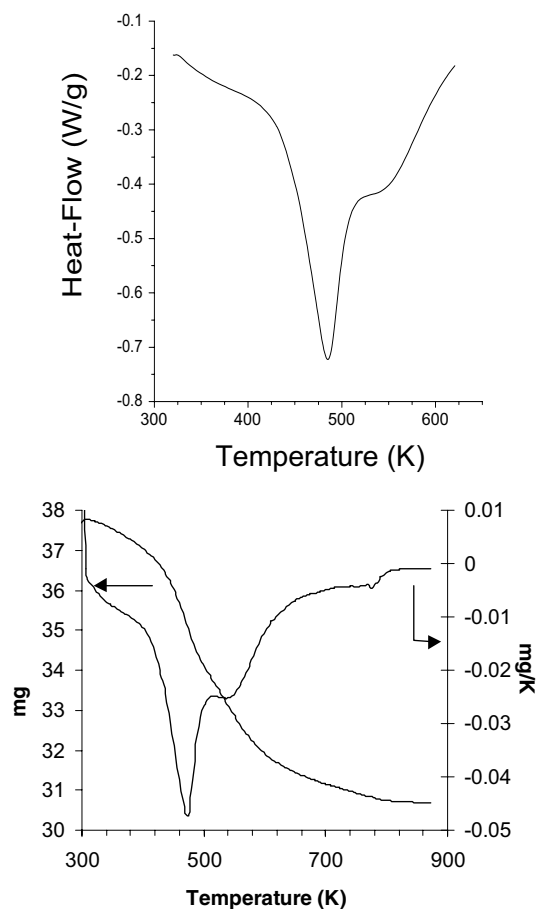


FIGURE 1. (a) Differential Scanning Calorimetry patterns of the stilbite sample; (b) TG and DTG curves of the stilbite sample.

seen at around 560 K. TG-DTG traces in the temperature range 325–825 K are also shown in Figure 1b. A total mass loss of about 18.61 wt% is observed in the temperature range 300–800 K and the dehydration was actually in two steps with a mass-loss of about 10.29 wt% in the temperature range 300–510 K and a further one of 8.15 wt% in 510–780 K range. These results are in good agreement with those reported by Gottardi and Galli (1985).

Infrared spectra collected for experiment 1 at selected temperatures are shown in Figure 2. In the spectrum collected at 300 K, the mode at 1653 cm^{-1} is due to water bending, and the corresponding stretching modes are observed at ca. 3260 , 3426 , and 3587 cm^{-1} . This structure is in concert with the complex structure proposed by Crupi et al. (2003). The asymmetric stretching modes of the TO_4 ($\text{T} = \text{Si}$ and Al) framework are around 1030 cm^{-1} with a shoulder extending to 1145 cm^{-1} . The symmetric stretching and bending modes for TO_4 are observed around 546 and 442 cm^{-1} . The spectral features observed are comparable to those in the infrared spectra reported by Li et al. (2000). The thermally induced variations in bending and stretching infrared modes of water groups were used to probe the dehydration mechanism.

The variations of the integrated area of the water modes is representative of the total water loss/gain. In this frame, it is informative to plot the variations of the total peak area of the water stretching (solid circles) and bending (triangles) measured in the wavenumber regions $3000\text{--}4100\text{ cm}^{-1}$ and $1590\text{--}1990\text{ cm}^{-1}$, respectively, with temperature. The results for experiment 1 are plotted in Figure 3a and show a gradual decrease of the normalized total peak area of the water stretching (solid circles) and bending (triangles) modes of stilbite with temperature, up to 775 K. The infrared features of water in stilbite are never recovered on cooling, indicating that the transformation is irreversible when heated to such temperatures.

A similar plot for experiment 2 is shown in Figure 3b. When the temperature reaches about 475 K, a loss of about 55% is clearly observed for the integrated areas of water modes. On cooling, a complete rehydration is clearly demonstrated by the increase in the total areas of such modes. Figure 3c represents the spectral

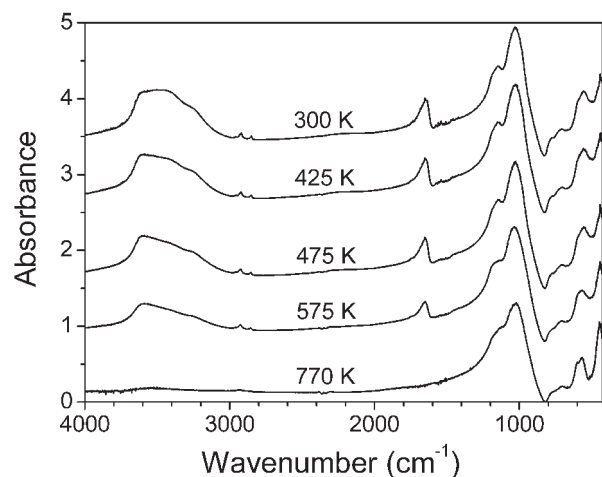


FIGURE 2. Background corrected IR spectra of stilbite collected at different temperatures of dehydration (300, 425, 475, 575, and 770 K) in the wavenumber range $400\text{--}4000\text{ cm}^{-1}$.

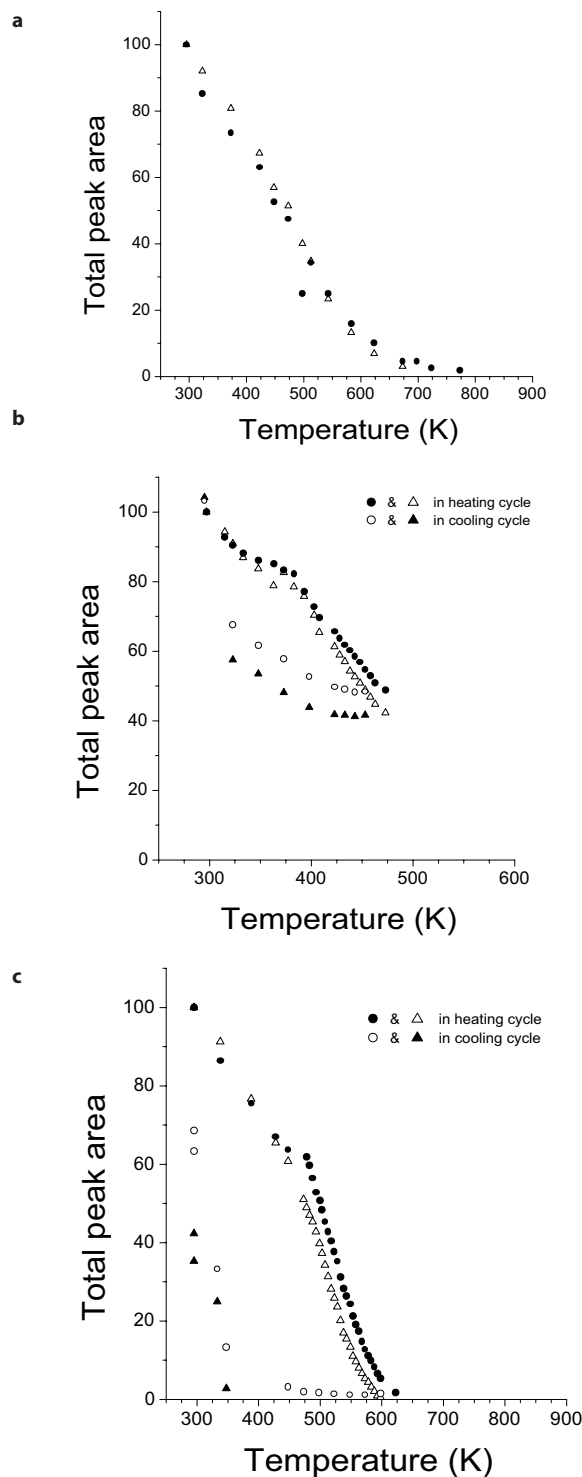


FIGURE 3. (a) Thermal variations of normalized total peak area of water stretching (solid circles) and bending (triangles) modes of stilbite; (b) Dehydration and rehydration behavior of stilbite in the temperature range 300 to 475 K. The symbols (solid circles and open triangles) represent observed behavior of stretching and bending modes during heating whereas the corresponding mode behavior is represented by open circles and filled triangles during cooling cycle; (c) Observed dehydration and rehydration of stilbite heated up to 630 K.

behavior observed in experiments 3, where the maximum temperature was 630 K. Around this temperature, the infrared modes due to water molecules have almost disappeared, indicating a total loss of water. On cooling, the bands regain about 33% (at 325 K) of their original intensity. A further 15% increase is observed when the sample is preserved for about 12 h in the laboratory. There was no further gain in the intensity even after preserving the sample over 30 days, indicating that the rehydration is only partial if the stilbite is heated up to 630 K.

The NIR spectral behavior of stilbite as a function of temperature was studied in experiment 4. The observed spectra at 300, 430, 450, 650, and 850 K are shown in Figure 4. The spectrum at 300 K has a band around 5233 cm^{-1} due to the combination of bending (1653 cm^{-1}) and stretching (3300–3600 cm^{-1}) modes. The other bands at 6825 and 7047 cm^{-1} are the overtone modes of the fundamental modes observed around 3426 and 3587 cm^{-1} . Similar spectral bands were reported by Cloutis et al. (2001) in the reflectance spectra of stilbite. As the temperature rises, these modes gradually become weaker, and the behavior is similar to the fundamental modes. The variations in the integrated peak areas in the wavenumber regions 6310–7500 cm^{-1} and 4585–5845 cm^{-1} for the overtone and combination modes, respectively, are plotted in Figure 5a. It is important to note the appearance of a mode around 4550 cm^{-1} that is clearly seen in the spectrum at 650 K in Figure 4. This band started appearing at 450 K, grew to a maximum around 650 K, and then decreased at higher temperatures. This mode clearly indicates the presence of Si-OH type bonding. The variation in the total peak area for this band in the wavenumber region 4310–4780 cm^{-1} is plotted in Figure 5b. The peak area is normalized with respect to the combination modes appearing at around 5233 cm^{-1} . From Figure 5b it is clear that the maximum peak area for this region is around 6–7%.

DISCUSSION

Cruciani et al. (1997) reported that the cell volume of the A phase of stilbite slightly decreases (0.64%) up to 420 K, whereas, a rather sharp decrease is observed (–3.24%) at 420 K. The cell volume of the B phase in the temperature range 430–520 K

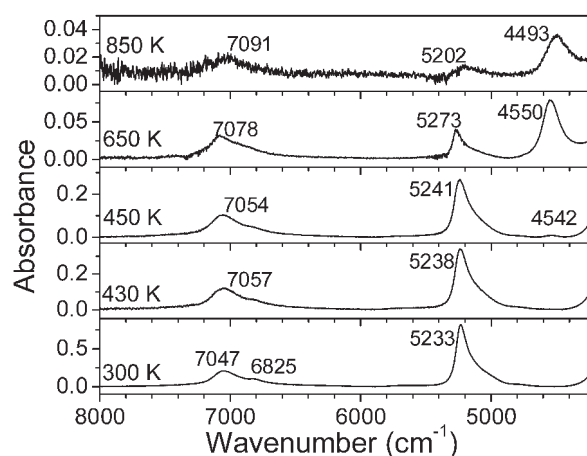


FIGURE 4. Background corrected spectra of stilbite collected at different temperatures of dehydration (300, 430, 450, 650, and 850 K) in the wavenumber region 4000–8000 cm^{-1} .

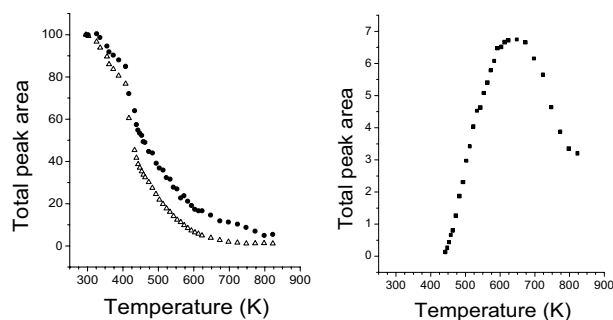


FIGURE 5. (a) Variations in the normalized peak-areas for the combinations (solid circles) and overtones (open triangles) of water molecules in stilbite; (b) Observed variation in total peak area of 4550 cm^{-1} , normalized to the area of the water combination mode around 5233 cm^{-1} .

showed an overall decrease of about –3.81% and these changes are attributed to the main phase transformation from monoclinic phase A to orthorhombic phase B. Phase B collapses at higher temperature (700 K). The observed FTIR behavior partly agrees with this picture. In the first run, we observed a smooth decrease in the peak areas of water modes (Fig. 3a) without a clear indication of the transformation from Phase A to phase B. Nearly half of the zeolitic water molecules are lost in Phase A as indicated by the decrease in the characteristic water modes (Fig. 3b). It is evident from Figure 1b that a mass loss of 10.29 wt% is observed in the temperature range 300–510 K and this corresponds to about 53% water molecules. Gottardi and Galli (1985) also reported similar observations. These water molecules, however, regained on cooling (see Fig. 3b). Again, Gottardi and Galli (1985) report that the remaining water molecules are lost during the temperature increase in phase B. This behavior is reflected by almost continuous variations in the peak areas of the water bending and stretching modes (Fig. 3a). However, the onset of Phase B around 420 K is clearly observed in the behavior of second-order modes plotted in Figure 5a in close agreement with Cruciani et al. (1997). We also observed no variations in the peak positions of the bending modes of the TO_4 network showing that the deformation of the framework is minor. Experiment 2 shows that the dehydration of Phase A is reversible over a short time scale. In fact, the peak areas of these bands regained their original values within 5 h on continuous cooling (Fig. 3b). Thus, it is possible to postulate that Phase A undergoes a fully reversible dehydration with no noticeable distortions of the framework.

The dehydration behavior of Phase B is rather different. In the near-IR region we observed the presence of a new band around 4550 cm^{-1} , which is due to silanol groups (Nyfeler and Armbruster 1998; Prasad and Sarma 2004). This band progressively became prominent at temperatures around 650 K (see Figs. 4 and 5b). Generally, hydrogen diffuses into the system to make a new linkage because of broken T-O-T bonds. In spite of the abundance and the spatial proximity of SiO_4 and H in minerals, they rarely bond to each other to form an SiOH (silanol) group. Hydrogen atoms usually bond to O atoms of larger coordination cations such as K, Na, Ca, Mg, Fe, Al, etc. (Nyfeler and Armbruster 1998). Stebbins et al. (1999) reported significant concentrations of Al-O-Al sites in naturally occurring zeolite (stilbite) and these have faster reactivity with H_2O vapor than Si-O-Si and Si-O-Al sites. In the IR fundamental

mode region, all the bands due to water molecules disappeared completely indicating a nearly total loss of water. From the TG analysis (Fig. 1b), a total mass of about 18.45 wt% corresponding to a loss of water molecules of about 96% was observed around 780 K. In experiment 3, the samples, which were heated up to 630 K, were slowly cooled back to room temperature. As depicted in Figure 3c, the rehydration process is rather slow. In about 5 h, only about 33 wt% increase could be observed down to 300 K. In about 72 hours, there was a further increase of about 15%, and no further significant intensity gain even after 30 days. In practice, over a short time period, Phase B regained only about 50% of the water molecules that were lost at 630 K. This observation agrees with the result that the rehydration of phase B is rather slow and occurs over a time span of years (Aumento 1966).

One more essential feature in the NIR region is the appearance of a mode around 4550 cm^{-1} . This band undoubtedly indicates the presence of a hydroxyl group attached to Si (i.e., an Si-OH bond: Prasad and Sarma 2004). A similar NIR band around 4524 cm^{-1} (2210 nm) was reported by Alberti et al. (1983) in heat-collapsed phases of barrerite and also by Hanke and Moller (1984) in some synthetic alkali zeolites. The evolution of this band is plotted in Figure 5b. The second-order modes show steep decreases in the total peak area around 448 K, and simultaneously the emergence of a new peak around 4550 cm^{-1} . Around this temperature Phase B is formed, corroborating previous observations (Gottardi and Galli 1985). However, as Phase B grows with temperature, the area of the peak at 4550 cm^{-1} also increases and reaches its maximum around 650 K (see Fig. 5b). On the other hand, modes due to H_2O continue to show a decreasing trend (see Fig. 5a). As reported by Cruciani et al. (1997) and Gottardi and Galli (1985), a progressive dehydration by about 26 molecules occurs in Phase B. Observed opposite trends for H_2O and OH groups, as shown in Figure 5, are a direct indication of decreasing H_2O and increasing OH. Moreover, the maximum peak area under the OH band is about 6–7% of the corresponding H_2O . The total concentration of the species is proportional to the ratio of the measured absorbance to the molar absorbance (ϵ^*). By assuming similar ϵ^* values as in rhyolites, i.e., $248 (\pm 24)$ and $341 (\pm 25)\text{ l}/(\text{mol}\cdot\text{cm}^2)$ respectively, for H_2O and OH (Newman et al. 1986), the maximum absorbance for the 4550 cm^{-1} peak around 650 K corresponds to about four hydroxyl groups. Our observation also supports the fact that the residual water molecules above 650 K are mostly in the form of hydroxyl groups (Aumento 1966; Gottardi and Galli 1985).

In conclusion, the results of this study confirm that the stilbite framework shows no distortions during the first stage of dehydration. However, during the dehydration of Phase B, framework distortion occurs and the breakage of T-O-T bonding causes the formation of hydroxyl groups as previously observed by Alberti et al. (1983). As clearly seen from Figures 4 and 5b, during the growth of Phase B, the mode around 4550 cm^{-1} (corresponding to Si-OH linkage) grows monotonously. Non-existence of Al-OH type linkage is characterized by the absence of the mode around 4795 cm^{-1} (Prasad and Gowd 2003) indicating that the probability of Al-O-Al linkage is very low in this stilbite sample. Moreover, the protonation occurs preferably at the Si-O site. In agreement with the literature data, a further increase of the temperature causes complete dehydration and breakage of T-O-T bonds and decomposition of Phase B.

ACKNOWLEDGMENTS

The authors sincerely thank the Director of the National Geophysical Research Institute, Hyderabad, for his encouragement, and permission to publish this paper. Helpful discussions with N.K. Thakur, D. Narayana Rao, and B. Sreedhar are greatly acknowledged. We thank G. Rama Rao of GSI Hyderabad for helping us with electron probe analysis. The authors are indebted to T. Armbruster, G. Cruciani, A. Gualtieri (A.E), and an anonymous reviewer for their comments and suggestions that improved the presentation of these results.

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MANUSCRIPT RECEIVED JUNE 14, 2004

MANUSCRIPT ACCEPTED FEBRUARY 11, 2005

MANUSCRIPT HANDLED BY ALESSANDRO GUALTIERI