

Study of Rehydration and Dehydration Behavior of Scolecite by In Situ Raman Spectroscopy

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Abstract

The study of structural changes of stretching and bending modes around 3000-4000cm⁻¹ and 700-1800cm⁻¹ in the temperature range of 299 to 503 K during the dehydration of naturally occurring scolecite was investigated using in-situ Raman spectroscopy. A Raman spectrum from 3000-4000cm⁻¹ was measured for a fibrous zeolite called scolecite to regulate the behavior of water molecules in the passages. The extending vibrations of H₂O molecules of scolecite are located between 3077 - 3600cm⁻¹ and bending vibrations occurred around 1666cm⁻¹. Gradual decrease in the intensity of the water modes at 1588cm⁻¹, 1659cm⁻¹, 1664cm⁻¹ in the bending region during dehydration indicates the loss of water molecules in scolecite is similar to the earlier reports by prasad et al.. In support of the above results a general phase transition for natural scolecite at 498K in the thermo gram of scolecite was observed. The zeolite group shows a broad range of functional phase transformations when they are increased to higher temperatures. We also observed the topical behaviour of H₂O molecules in zeolite that is loss of water and sediment mass loss with change of temperature using DSC and Raman Spectroscopic studies. We found that the transition temperature of the scolecite sample is found at around 476K using DSC. The two-step behaviour is very well observed by thermal analysis and shift 1664cm⁻¹ to 1646cm⁻¹, absence of 1588 cm⁻¹ mode at 498K indicates the loss of water molecules studied. As there will be no practical mass change insignificantly, Undistinguished mass loss corresponds to little or no slope in the TGA trace of the specimen.

Keywords: Dehydration mechanisms, scolecite, stretching, bending modes, water loss, raman spectroscopy

INTRODUCTION

The Zeolites are crystalline solids structures made of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water and or small molecules may reside. These are crystalline aluminosilicates with open three dimension structure built of Si-O tetrahedron and tetrahedral aluminium oxide linked to each other by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimension [3,7]. The crucial feature of zeolites is that their frameworks are made up of four-coordinated atoms forming tetrahedra. These tetrahedra are linked together by their corners and the framing [11]. The cementation contribution to shear strength of clay or zeolite decreases with increase in specific surface area of soil minerals which helps in Gas Hydrates [11]. The different H₂O molecules can have slightly different O-H and O O bond lengths, as described by Artioli et al [10].

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The zeolite building block demonstrates a wide range of constitution phase transformations when they are increased to higher temperatures. Our aim

is to observe the local behavior of H₂O molecules in scolecite on increase of the temperature using DSC and Raman spectroscopic studies.

EXPERIMENTA

Sample Preparation

The samples were collected from naturally occurring zeolite in the area around Poona, India. The materials were used without further purification. Suitable samples were cut from a larger crystal for NIR studies. [12] Whereas the same powdered samples were used in lesser quantity for other investigations using Raman spectroscopy. Though the shaping kinetics and complete hydrate conversion in permeable sediments are also analysed in previous studies using these sediments which in turn helps in Gas hydrates synthesis [9].

Thermal Analysis

The thermogravimetric analysis (TGA & DTG) was performed on MT-TGA/ Single Differential Thermal Analysis 851 system using 11.551 mg of zeolite sample. Measurements were carried out in the temperature collection 303–723 K with a heating rate of 8 °C/min in Osmania University.

In-Situ Raman Studies: In order to obtain a better understanding of the molecular bonding during the structural transformations in scolecite, we have investigated behaviour and structural modifications in zeolites of second order modes of water molecules occurring in the range 3000 to 4000 cm⁻¹. Raman spectra are collected at different stages of dehydration at 298K, 373K, 448K and 498K temperatures as made in Figure 1(a,b). The spectra of Raman for scolecite at different temperatures from 298K to 498K while Warming in the stretching region and in the bending region are shown in the Figure 1 (a,b)

Data Collection

Raman spectra for the scolecite sample at low temperatures from 93K to 298K and again 298K to 503K was collected both in low frequency range (100cm⁻¹ – 2000cm⁻¹) and high frequency range (3000cm⁻¹ – 4000cm⁻¹). They illustrate intense O-H stretching and H₂O bending modes resulting from the hydrogen bonded water molecules in the channels. The Oxygen-Hydrogen broadening modes and bending modes for scolecite are obtained with the help of dehydration and rehydration cycles from room temperature 298K to 93K by slaking the cells to liquid nitrogen environments. [1] The temperature was varied in steps typically at a amount 0.5°/ min and the data was collected for every five minutes of interval. [1] Only during the accumulation the laser was focused onto a spot on the sample with a fifty multiple lens. Although occasionally the focus was adjusted for a better sign eminence, proper care was taken not for implication away from the initial point. Complete disintegration of the hydrate was expected when it became unbearable to record the distinguishing Raman features from the sample. To determine the integrated intensities, Lorentz multi-peak curve fitting using GRAMS software was applied to the Raman array obtained. From the fitted curves, the ratio of the merged intensity level of large to small cages of the Raman spectrum was measured.

Stahl and Hanson [5]. studied the phase changes in scolecite using actual time powder synchrotron X-Ray diversion studies and conveyed that it transforms to meta scolecite initially at 489K, by desiccating water coordinated with Ca atom^{5,6}. From the studies of joshi 1,4 using FTIR [6]., there are no changes in OH stretching and H₂O bending modes below 573K. However, they reported variations only above 573K. contrary to the mechanism proposed for the transformations by stahl & Hanson^{5,4}. The FTIR spectrum recorded in the wave number region 3000-3600cm⁻¹ has bands around 3587cm⁻¹, 3507cm⁻¹, 3409cm⁻¹, 3327cm⁻¹, 3232cm⁻¹ and two shoulder peaks at 3145cm⁻¹ & 3054cm⁻¹ [4]. Using Raman spectroscopy, we found that the intensity of five bands at 3575 cm⁻¹, 3503 cm⁻¹, 3416 cm⁻¹, 3328cm⁻¹, 3231cm⁻¹ decrease up on heating from 448K to 498K. The bands are widened and strongly coincided at T>473K in match with Stahl and Hanson [5]. The zeolite group shows a wide range of structural phase transformations when they are increased to higher temperatures. Our aim is to observe the local behaviour of H₂O molecules in scolecite with increase of temperature using DSC and Raman Spectroscopic studies.

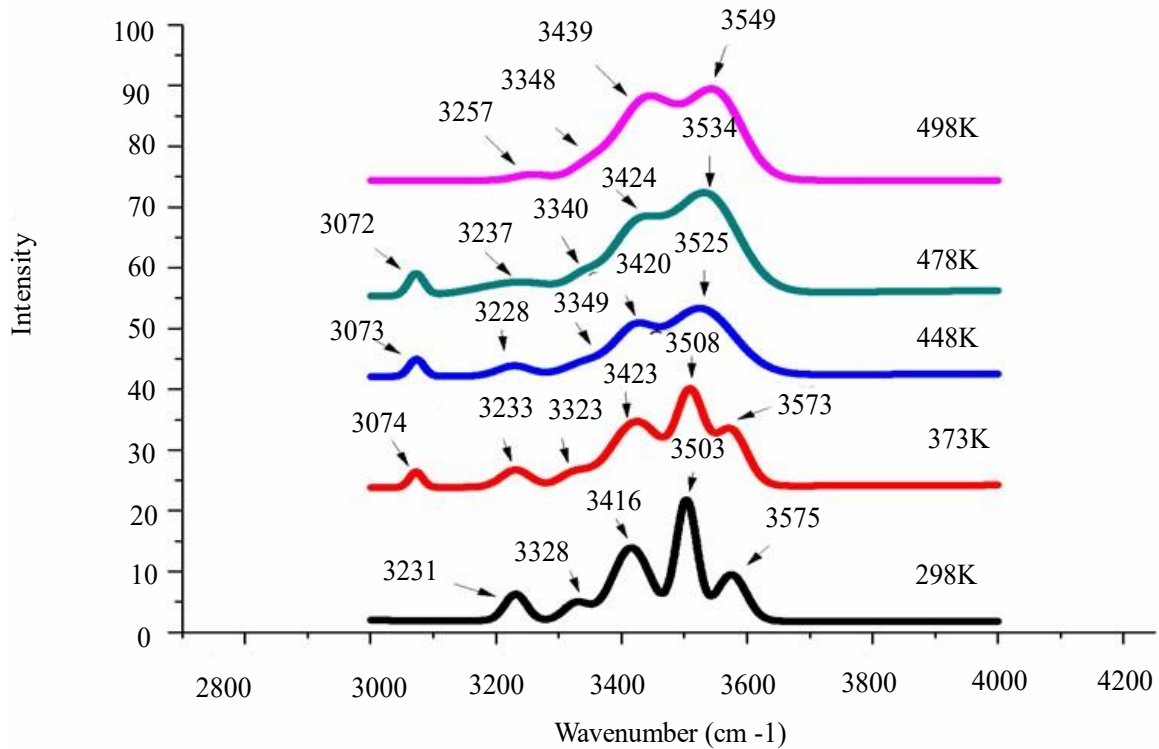


Figure 1. (a) Raman spectra for scolecite at different temperatures from 298K to 498K while warming in the stretching region.

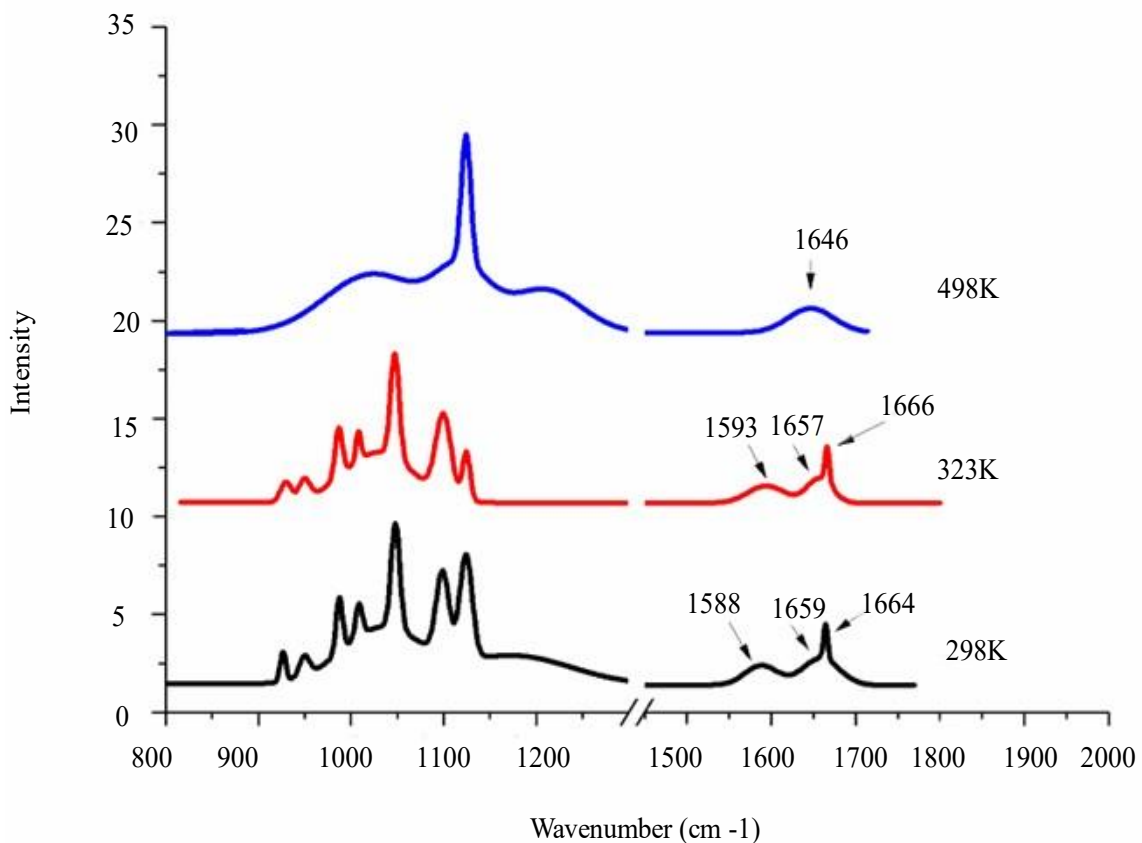


Figure 1. (b) The fig shows Raman spectra of scolecite in the bending region.

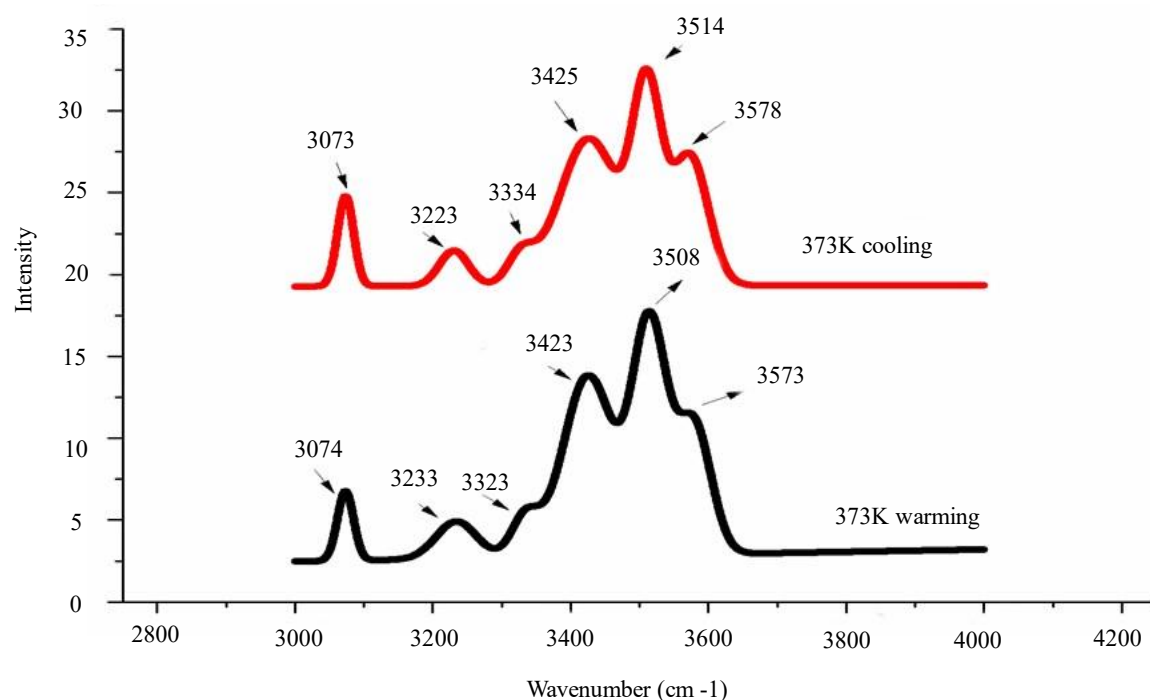


Figure 1. (c) Raman spectra collected at 373K while warming and cooling.

We have investigated dehydration behavior and structural modifications of the zeolites of second order kinds of water fragments occurring in the series 3000-4000 cm^{-1} . Raman spectra were collected at different stage of dehydration at 298K, 373K, 448K, 478K and 498K temperatures as shown in the Figure 1(a). Raman spectra show intense O-H stretching and H_2O bending modes derived from the H bonded water molecules in the channels. For scolecite at 373K, six 3573 cm^{-1} , 3508 cm^{-1} , 3423 cm^{-1} , 3323 cm^{-1} , 3233 cm^{-1} , 3074 cm^{-1} . O-H stretching modes and three bending modes are observed at $1588, 1659, 1664\text{ cm}^{-1}$ in Raman spectra as shown above in 1(b). while increasing the temperature from 298K to 478K, at 373K in stretching region a new mode has appeared at 3074 cm^{-1} and the Same mode has reappeared while cooling as shown in the Figure 1(c).

RESULTS AND DISCUSSION

The two-step dehydration behaviour is very well observed with least $300\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$ in inert gases without structural changes or strength loss, which can be analyzed by TGA. In our experiments, scolecite sample of 11.551 mg is taken, for evaluating the thermal stability of the material. Temperature range from 303K to 723K for this sample has been taken for thermal stability. If the species is thermally stable, there will be no observed mass change. Here in our experiments, negligible mass loss corresponds to tiny or no slope in the TGA trace. TGA also gives the top use temperature of a material. Beyond 723K temperature from previous studies by Prasad et al, the material will begin to degrade. As there will be no practical mass change. Insignificant mass loss corresponds to little or no slope in the TGA trace. The Average total mass loss is about 6% and loss increased to 9% when it reaches to 780K. with a corresponding water loss as shown in the figure 2 (a,b). These results are in good agreement with those reported by Gottardi and Galli (1985).

The appearance of this 3074 cm^{-1} mode may be because of the composition or any impurity to the calcium in the frame work. During warming because of dehydration of water molecules, this peak has come at 373K, and while cooling as the water molecules cannot be immediately regain to the surround completely, so the peak is observed until room temperature. The anti stokes combination modes 3074 cm^{-1} and 3233 cm^{-1} at 373K change by (kolesov & Geiger) [7]. A possible explanation for this is that the translational condition related with three H_2O molecules

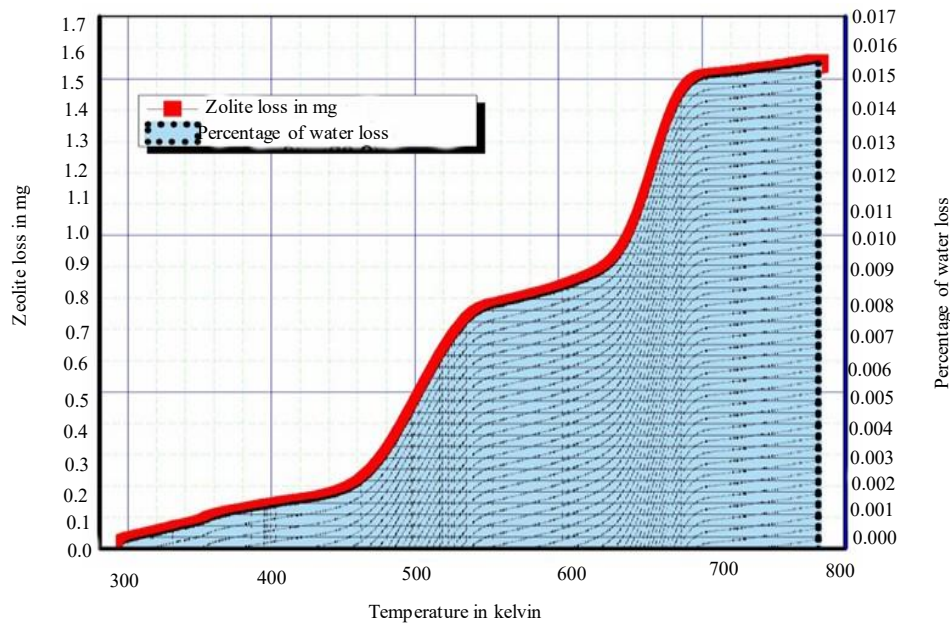


Figure 2. (a) Mass and water loss in zeolite using TGA.

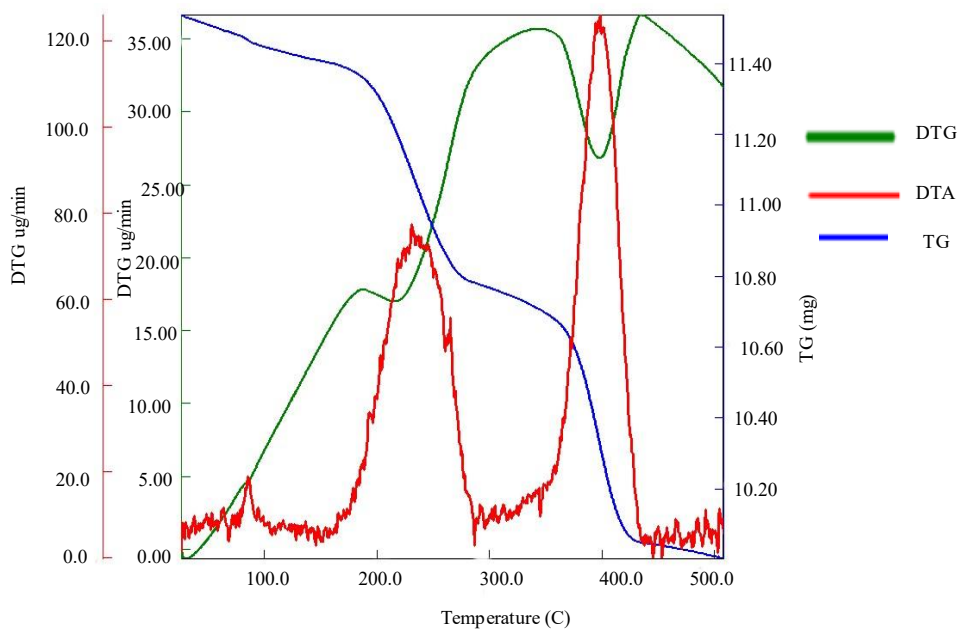


Figure 2. (b) DTG ,DTA and TG curves of zeolite.

Are coupled and a reduction in concentration of the W2 H₂O grains causes a change in the translational energies linked with W1 and W3 H₂O molecules as shown in Figure 3 [7]. The dehydration and rehydration behavior of scolecite was examined by Raman measurements of the Oxygen and Hydrogen stretching modes at temperatures from 298K-498K. Raman spectra, obtained over this range of temperature, permit one to obtain a better understanding of inner surface, H₂O-molecule behaviour in micro porous silicates and the behaviour of hydrogen bonding.

The high temperature Raman spectra, in comparison to room temperature show four modes at 3549cm⁻¹, 3439cm⁻¹, 3348cm⁻¹, 3257cm⁻¹ at 498K as shown in the Figure 1(a). 3575cm⁻¹ mode at room temperature shifts to 3549 cm⁻¹ on increase of temperature to 498K. Again while cooling from 498K to 298K there is a shift towards higher side i.e, from 3549 cm⁻¹ to 3576 cm⁻¹

The 3503cm⁻¹ mode at 298K shifts towards lower wavelength side at 498K (i.e 3439 cm⁻¹). 3416cm⁻¹ mode shifts towards higher wavelength side with the increase of temperature from 298K to 498K. At 498K, 3439cm⁻¹ mode actually consists of two overlapped bands which include 3503 cm⁻¹ & 3416 cm⁻¹ showing the behavior similar to the studies by kolesov &gieger [7], 2006. Again while cooling the peak has come to the normal position. The 3231 cm⁻¹ mode and a shoulder peak at 3232 cm⁻¹ which appeared at room temperature also shifts towards the higher wave number side to 3257cm⁻¹ at 498K as shown in fig 4. This is because of the modes which are located between 3200cm⁻¹ and 3600 cm⁻¹ are assigned to three water molecules which stretch rise to dense system of interrelating vibrations of stretching-stretching, Stretching-Translational, Translational –Translational vibrations of water modes [7].

Gradual decrease in the intensity of the water modes at 1588cm⁻¹,1659cm⁻¹ ,1664cm⁻¹ as shown in the Figure 1(b), in the bending region shows the loss of water molecules which shows comparable results with earlier IR studies done by kolesov and Geiger & Prasad et al.[7,4]. Because of the increase of temperature, the thermal vibrations that are caused between H-O-H increases and there by force constant increases so the wave number shifts towards the higher order [4,7]. The 1646 cm⁻¹ mode at 498K is the most intense in the bending region of raman spectrum as shown in Figure 1(b),which is obtained by combining of two intense bands 1664cm⁻¹ and 1659cm⁻¹ at room temperature. There is a shift in this band from 1664cm⁻¹ to 1646cm⁻¹. The disappearance of 1588 cm⁻¹ mode at 498K indicates the loss of water molecules which is consistent with high temperature in- situ IR measurements (Prasad &Prasad 1997) [4]. The intensity of five bands at 3575 cm⁻¹,3503 cm⁻¹,3416 cm⁻¹,3328cm⁻¹ and 3231cm⁻¹ at room temperature decrease rapidly up on heating from 448K-498K. The bands are broadened and strongly overlapped at T>200°C in match with Stahl and Hanson1994[5]. The first phase transition of scolecite occurred at 203.440C using our DSC studies are shown in Figure 5.

The dehydration of scolecite starts at approximately 323K with expulsion of one of the three water molecules, labeled as W2 in crystal structure fig 3 From the earlier results that were obtained by kolesov and gieger[7], W2(H3-O12-H4) molecule is the first molecule that begins to diffuse out of the crystal, followed by W1 and W3 at higher temperatures(Gottardi and Galli 1985[2];stahl and Hanson 1994[5]).Hence the band 3328 cm⁻¹ at room temperature in our raman spectra shows the three crystallographically distinct H₂O molecules in each cavity have different H –bond behavior in crystal hydrates. The 3 distinct H₂O molecules in each cavity have different hydrogen union distances with neighboring Oxygen atoms from Kvick et al.1985[8]. similar to the above results we found that the transition temperature of the scolecite sample is at 476K using DSC is shown in Figure 5. For analysis and mode assignments , we have used the notation for the atoms and bonds of the water molecules as found in Kvick et al.(1985)[8]and the structural convention from stucken schmidt et al(1997) [12].

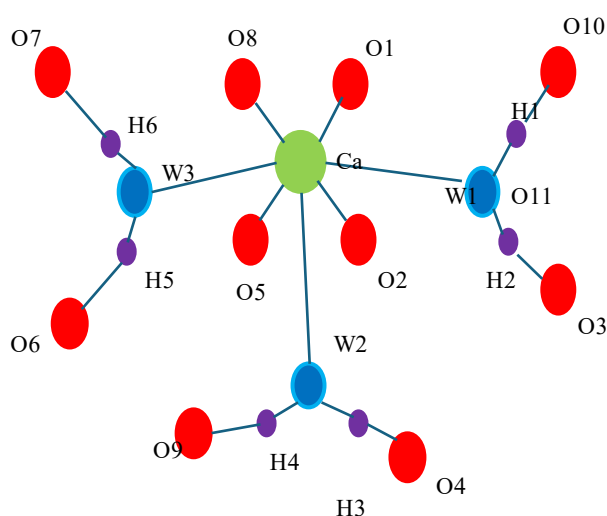


Figure 3. The crystal structure of scolecite [7].

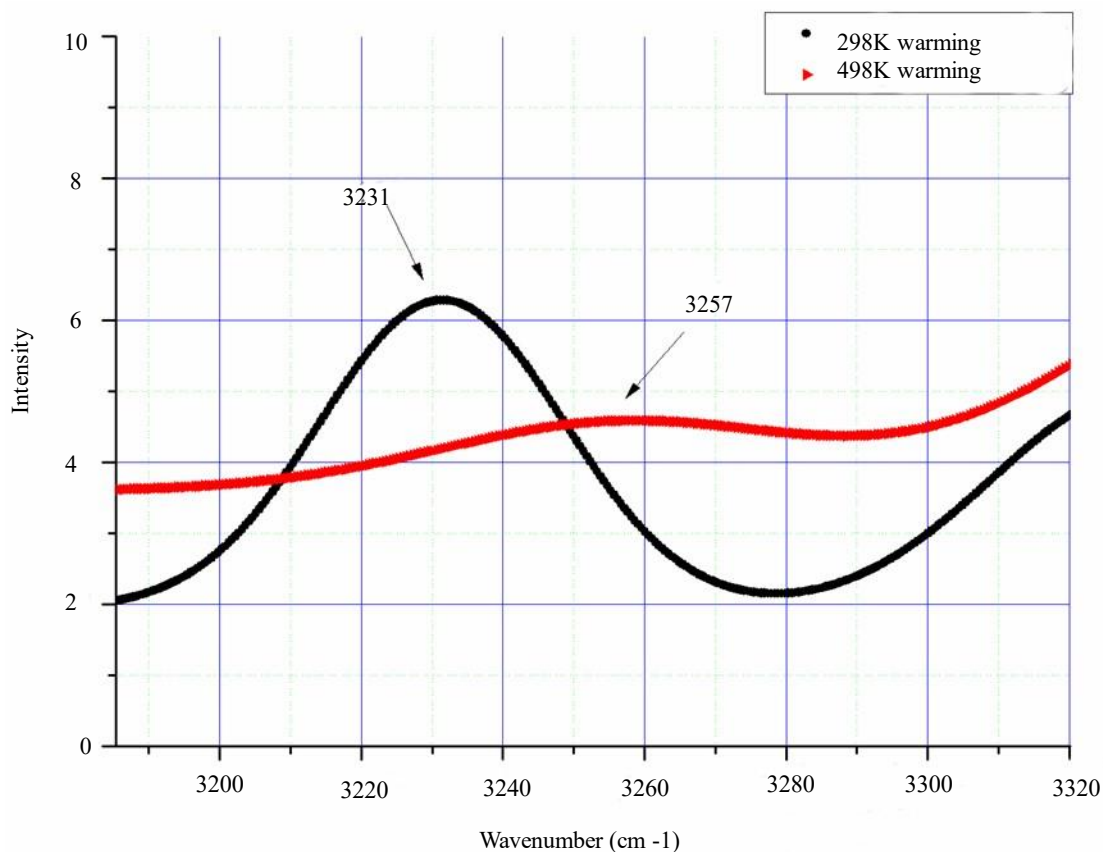


Figure 4. This Figure shows the shifting of 3231 cm^{-1} mode to 3257 cm^{-1} on dehydration from 298K to 498K in Raman spectra.

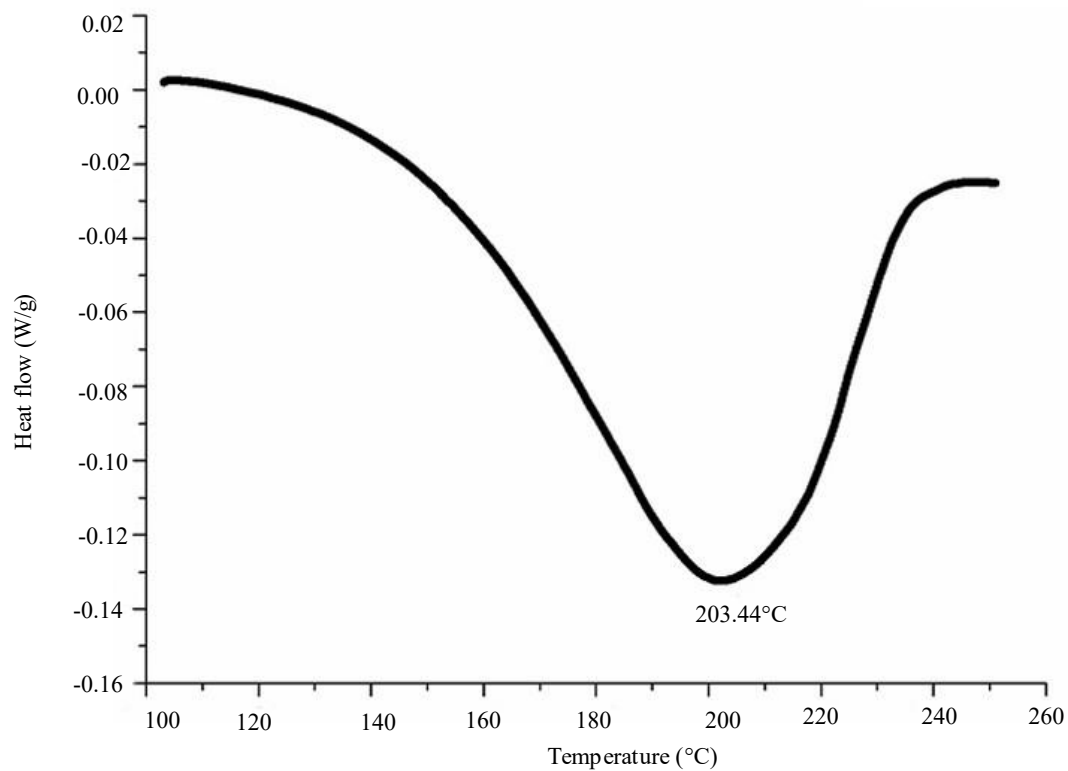


Figure 5. The above figure indicates the transition temperature is at 203.44 $^{\circ}\text{C}$ using DSC.

CONCLUSIONS

We have studied the partial dehydration behavior due to Calcium associated with three H₂O molecules in scolecite, which causes conversion to Meta scolecite. The two-step behaviour is very well observed by thermal analysis and shift 1664cm⁻¹ to 1646cm⁻¹, absence of 1588 cm⁻¹ mode at 498K indicates the loss of water molecules studied in this paper by in-situ Raman studies are in good agreement with previous studies done by Prasad et al for high temperatures using in-situ IR dimensions

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