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The dehydroxylation of basic aluminum sulfate: An infrared emission spectroscopic study

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Abstract

The tridecameric aluminum polymer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ was prepared by forced hydrolysis of Al^{3+} up to an OH/Al molar ratio of 2.2. Upon addition of sulfate, the tridecamer crystallized as the monoclinic basic aluminum sulfate $Na_{0.1}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}$. The dehydroxylation of the basic aluminum sulfate has been studied by Fourier transform in-situ infrared emission spectroscopy over a temperature range of 200° to 750°C at 50°C intervals. The spectrum is characterized by the sulfate ν_1 (1024 cm^{-1}), ν_3 doublet (1117 and 1168 cm^{-1}) and the ν_4 doublet (568 and 611 cm^{-1}) modes. Furthermore, minor bands assigned to nitrate are observed. Upon heating from ≈350° to 400°C major changes are observed, especially in the bandwidth and band intensities. The bands in the hydroxyl stretching region due to the Al_{13} group disappear, whereas the bands around 1050 cm^{-1} display various changes in bandwidths, intensities and positions associated with the dehydration and dehydroxylation of the basic sulfate and the changing of the structure into an aluminum oxosulfate. The nitrate bands diminish upon heating. © 1998 Elsevier Science B.V.

Keywords: Al_{13}; Basic aluminum sulfate; Dehydroxylation; Infrared emission spectroscopy; Tridecamer

1. Introduction

Forced hydrolysis of aluminum solutions by the addition of base solutions, or homogeneous hydrolysis by the decomposition of urea, is known to result in the formation of a large number of complexes. One of the most studied complexes is the tridecameric complex or Al_{13}, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ [1–3]. This tridecamer can be visualized as a central tetrahedral AlO_4, surrounded by 12 aluminum octahedrals in the form of a cage. Besides the use of this polymer in the preparation of pillared clays molecular sieves and heterogeneous catalysts [4–8], it has also commercial value because of its antiperspirant activity and its ability to control the viscosity of kaolinite clay [9].

Johansson [10–12] and Johansson et al. [13] were the first who described the precipitation of two different basic aluminum sulfates, both containing the tridecameric aluminum building unit linked by hydrogen bonding to the oxygen atoms of the sulfate groups. The sodium-containing aluminum sulfate crystallized in the cubic system, whereas the sodium-free sulfate crystallized in the monoclinic system.

In more recent papers, Kloprogge et al. [14,15] described the precipitation of monoclinic basic aluminum sulfate with a small amount of sodium.

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Based on their chemical analyses by ICP-AES, they reported a chemical composition per unit cell of $Na_{0.1}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}\cdot 9H_2O$. ^{27}Al solid-state magic-angle spinning nuclear magnetic resonance spectroscopy showed that the tridecameric units were still present in the crystal structure. Thermogravimetric analyses indicated that the structure is completely stable up to 80°C, although 9 mol of physically adsorbed water were lost. Between 80° and 360°C, the aluminum sulfate crystal gradually decomposed, losing its 12 water and 24 hydroxyl groups. At this stage the aluminum sulfate became X-ray amorphous. Between 360° and 950°C, with a maximum between 880° and 950°C, the SO_3 groups are removed, leaving the aluminum oxide.

The aim of this paper is to describe the thermal degradation of monoclinic basic aluminum sulfate by using a relatively scarcely used technique known as infrared emission spectroscopy (IES) [16–19]. The major advantages of IES are that the discrete vibrational frequencies emitted by thermally excited molecules are measured, in situ, on samples at elevated temperatures. This technique overcomes the problems associated with the use of normal infrared spectroscopic techniques like the use of pressed KBr tablets. Furthermore, it removes the difficulty of heating the sample to a specific temperature followed by quenching before any measurements can be performed, while assuming that no phase changes occur upon cooling. IES actually measures the spectra while the dehydroxylation reactions in the aluminum sulfate are in progress.

2. Experimental techniques

2.1. Basic aluminum sulfate

The synthesis and characterization of the monoclinic basic aluminum sulfate, used in this study, have been extensively studied by Kloprogge et al. [2,14,15]. The tridecameric aluminum polymer was obtained by forced hydrolysis of a 0.5 M aluminum nitrate solution with a 0.5 M sodium hydroxide solution until an OH/Al molar ratio of 2.2 was reached. Next, the basic aluminum sulfate was precipitated by the addition of the appropriate amount of 0.5 M sodium sulfate and aged for 42 days before removal from the solution. Crystals collected from the wall of the container were shown to be phase pure.

2.2. Infrared emission spectroscopy

FT-IR emission spectroscopy was carried out on a Digilab FTS-60A spectrometer, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have already been published elsewhere [16].

Approximately 0.2 mg of the basic aluminum sulfate was spread as a thin layer on a 6-mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. The infrared emission cell consists of a modified atomic

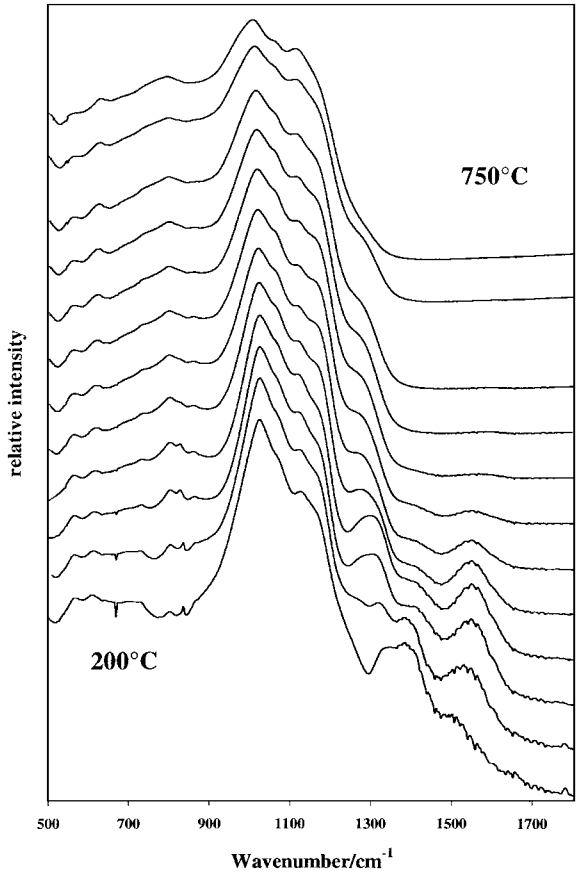

Fig. 1. The infrared emission spectra of basic aluminum sulfate over the 500 to 1800 cm^{-1} range and from 200° to 750°C at 50°C intervals.

absorption graphite rod furnace, which is driven by a thyristor-controlled AC power supply capable of delivering up to 150 A at 12 V. A platinum disk acts as a hot plate to heat the basic aluminum sulfate sample and is placed on the graphite rod. An insulated 125-μm type R thermocouple was embedded inside the platinum plate in such a way that the thermocouple junction was <0.2 mm below the surface of the platinum. Temperature control of ±2°C at the operating temperature of the aluminum sulfate sample was achieved by using a Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple.

The design of the IES facility is based on an off-axis paraboloid mirror with a focal length of 25 mm mounted above the heater which captures the infrared radiation and directs the radiation into the spectrometer. The assembly of the heating block and platinum hot plate is located such that the surface of the platinum is slightly above the focal point of the off-axis paraboloid mirror. By this means, the geometry is such that ≈3-mm diameter area is sampled by the spectrometer. The spectrometer was modified by the removal of the source assembly and mounting a gold-coated mirror, which was drilled through the center to allow the passage of the laser beam. The mirror was mounted at 45°, which enables the IR radiation to be directed into the FT-IR spectrometer.

In the normal course of events, three sets of spectra are obtained: firstly, the black-body radiation over the temperature range selected at the various temperatures; secondly, the platinum plate radiation is obtained at the same temperatures; and, thirdly, the spectra from the platinum plate covered with the sample. Normally, only one set of black-body and platinum radiations is required. The emittance spectrum at a particular temperature was calculated by subtraction of the single-beam spectrum of the platinum back-plate from that of the platinum+sample, and the result ratioed to the single-beam spectrum of an approximate black body (graphite). This spectral manipulation is carried out after all the spectral data has been collected.

The emission spectra were collected at intervals of 50°C over the 200–750°C range. The period between scans (while the temperature was raised to the next hold point) was ≈100 s. It was considered that this was sufficient time for the heating block and the powdered sample to reach a temperature equilibrium. The spectra were acquired by co-addition of 64 scans for the whole temperature range (approximate scanning time 45 s), with a nominal resolution of 4 cm^{-1}.

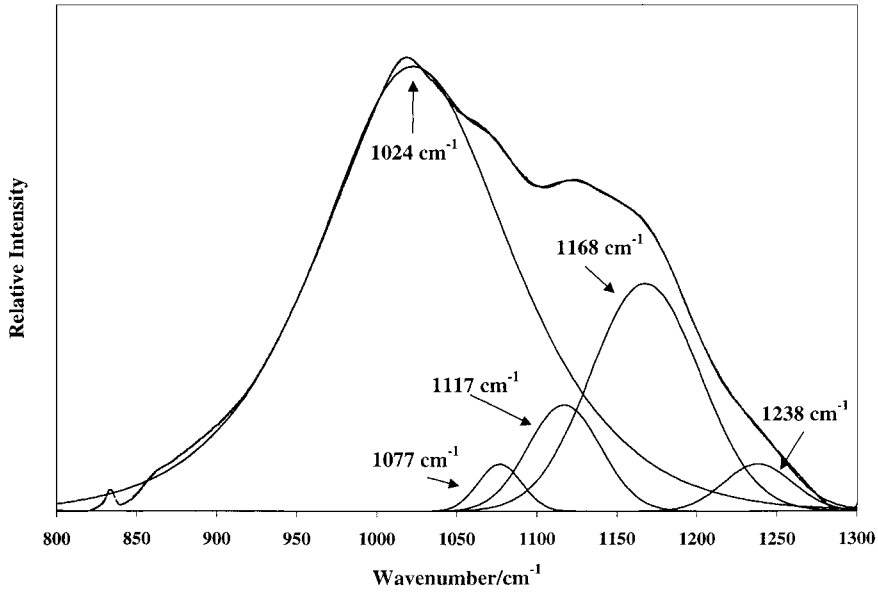

Fig. 2. Band-component analysis of the IES spectrum of basic aluminum sulfate at 200°C in the 800–1300 cm^{-1} region.

Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used, then the spectra become difficult to interpret because of the presence of combination and overtone bands. Spectral manipulation such as baseline adjustment, smoothing and normalization was performed using the Spectracalc software package (Galactic Industries, NH). Band-component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values >0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2>0.995.

3. Results and discussion

The emission spectra of the basic aluminum sulfate in the 500–1800 cm^{-1} region obtained at 50°C intervals from 200° to 750°C are shown in Fig. 1. The 200°C spectrum at the bottom of Fig. 1 clearly shows a broad complex band around 1100 cm^{-1} with recognizable bands at 1168 (shoulder), 1117, 1077 and 1024 cm^{-1} with a very weak second shoulder at 1238 cm^{-1} based on band-component analysis (Fig. 2). A broad band at 1350 cm^{-1} seems to be made up of two different bands at 1331 and 1386 cm^{-1}, respectively. Another band is observed at 1502 cm^{-1}. The absence of a water band around 1635 cm^{-1} is noteworthy, as it was expected based on the initial crystal composition containing nine water molecules. However, the heating to 200°C seems to be enough to remove all crystal water in agreement with the TGA data indicating dehydration to take place below 80°C [14].

The band at 1502 cm^{-1}, while increasing in intensity, shifts ≈35 cm^{-1} towards higher wave numbers (red shift) during heating to 400°C. At 550°C, this band disappeared altogether along with the 1386 cm^{-1} band. Also, the minor bands, visible at 867, 834 and 731 cm^{-1}, disappear upon heating to 550°C. These bands are interpreted as belonging to a minor amount of nitrate in the crystal structure of the basic aluminum, which was also proven in a recent Raman microscopy study of this material [20], although the amount of nitrate was too small to be detected in the chemical analyses reported earlier by Kloprogge et al. [14].

In the lower frequency region, three more bands are visible at 801, 611 and 568 cm^{-1}. Although the band at 801 cm^{-1} shifts towards 782 cm^{-1} upon heating, it still remains visible at 750°C. The two bands at 611 and 568 cm^{-1} are interpreted as the $\Delta\nu_4$ doublet of the sulfate, comparable to the 640 and 620 cm^{-1} doublet of sodium sulfate. The $\Delta\nu_4$ of 43 cm^{-1} is larger than the $\Delta\nu_4$ of the sodium sulfate and is more comparable with the $\Delta\nu_4$ of 39 cm^{-1}, known for aluminum sulfate [21].

Upon heating, the shoulder at 1257 cm^{-1} becomes more clearly visible in the 250°C spectrum, whereas the 1331 cm^{-1} band shifts to 1315 cm^{-1}. Further heating to 300°C results in a combining of both bands

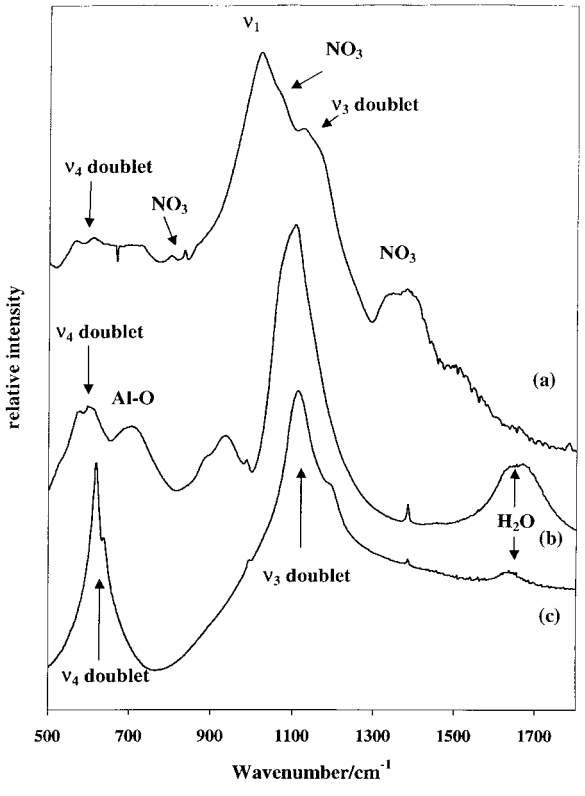

Fig. 3. (a) The infrared emission spectrum of basic aluminum sulfate, and the IR absorption spectra of (b) $Al_2(SO_4)_3{\cdot}xH_2O$ and (c) $Na_2SO_4{\cdot}xH_2O$ over the 500–1800 cm^{-1} range.

into a new broad band at 1281 cm^{-1}, which remains visible as a shoulder up to 750°C. Based upon comparison with hydrated aluminum- and sodium sulfate (Fig. 3), these bands are interpreted as the non-degenerate ν_1 or else as the triplet ν_3 of the sulfate group [22], although the ν_3 is normally observed as a doublet [23], or the doublet ν_3 of the sulfate group together with a nitrate band at 1077 cm^{-1}. Based on a comparison with the Raman spectrum, which shows a sharp band at 1067 cm^{-1} of this basic aluminum sulfate and the fact that normally a doublet is observed, the last option is preferred [20]. The band component analysis of the final product after heating to 750°C is shown in Fig. 4. Two major bands can be distinguished at ≈994 and 1133 cm^{-1}, belonging to the ν_1 and ν_3 of the sulfate group with three very minor bands at 1054, 1181 and 1274 cm^{-1} with relative band intensities of 0.2, 1.0 and 0.4%, respectively.

Thermogravimetric analysis has shown that the basic aluminum sulfate dehydrates and dehydroxylates below 350°C [14]. This is also reflected in the changes, below 400°C, in position, bandwidth and relative band intensity as visualized in Fig. 5. The two bands at 1024 and 1077 cm^{-1} reveal a blue shift of 23 and 30 cm^{-1} over the temperature range from 200°C to 750°C, while the two bands at 1117 and 1168 cm^{-1} show a red shift of 16 and 13 cm^{-1}, respectively (Fig. 5(a)). The bandwidths of the 1024 and 1168 cm^{-1} bands show a strong decrease in width up to 350°C, indicating that the sulfate positions in the crystal structure become better defined upon dehydroxylation, even though heating stage X-ray diffraction has shown that the dehydroxylated basic aluminum sulfate becomes X-ray amorphous [14]. This is probably more strongly reflected in the continuous increase in the bandwidth of the 1024 cm^{-1} band from 350°C up to 700°C. In contrast, the 1117 cm^{-1} band shows an increase in bandwidth up to 250°C, remains constant till 300°C and then shows a continuous increase till ≈500°C (Fig. 5(b)). A similar contrasting behavior can also be observed in the relative band intensities of the 1024 and 1168 cm^{-1} bands, on the one hand, and the 1117 cm^{-1} band, on the other hand (Fig. 5(c)).

The 1077 cm^{-1} band reveals an increase in bandwidth till 300°C, followed by a decrease up to 450°C. This can be explained by the fact that the nitrate group is lost from the structure in this temperature interval. Upon denitration, the nitrate group first loses its precise coordination within the structure causing the broadening, followed by the removal of the nitrate causing the narrowing when the amount of nitrate

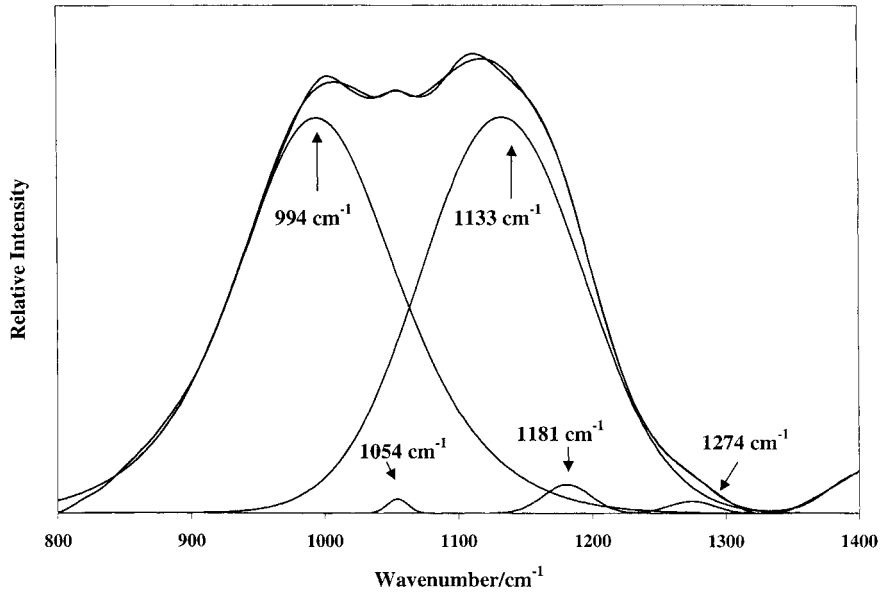

Fig. 4. Band component analysis of the IES spectrum of basic aluminum sulfate at 750°C in the 800-1400 cm^{-1} region.

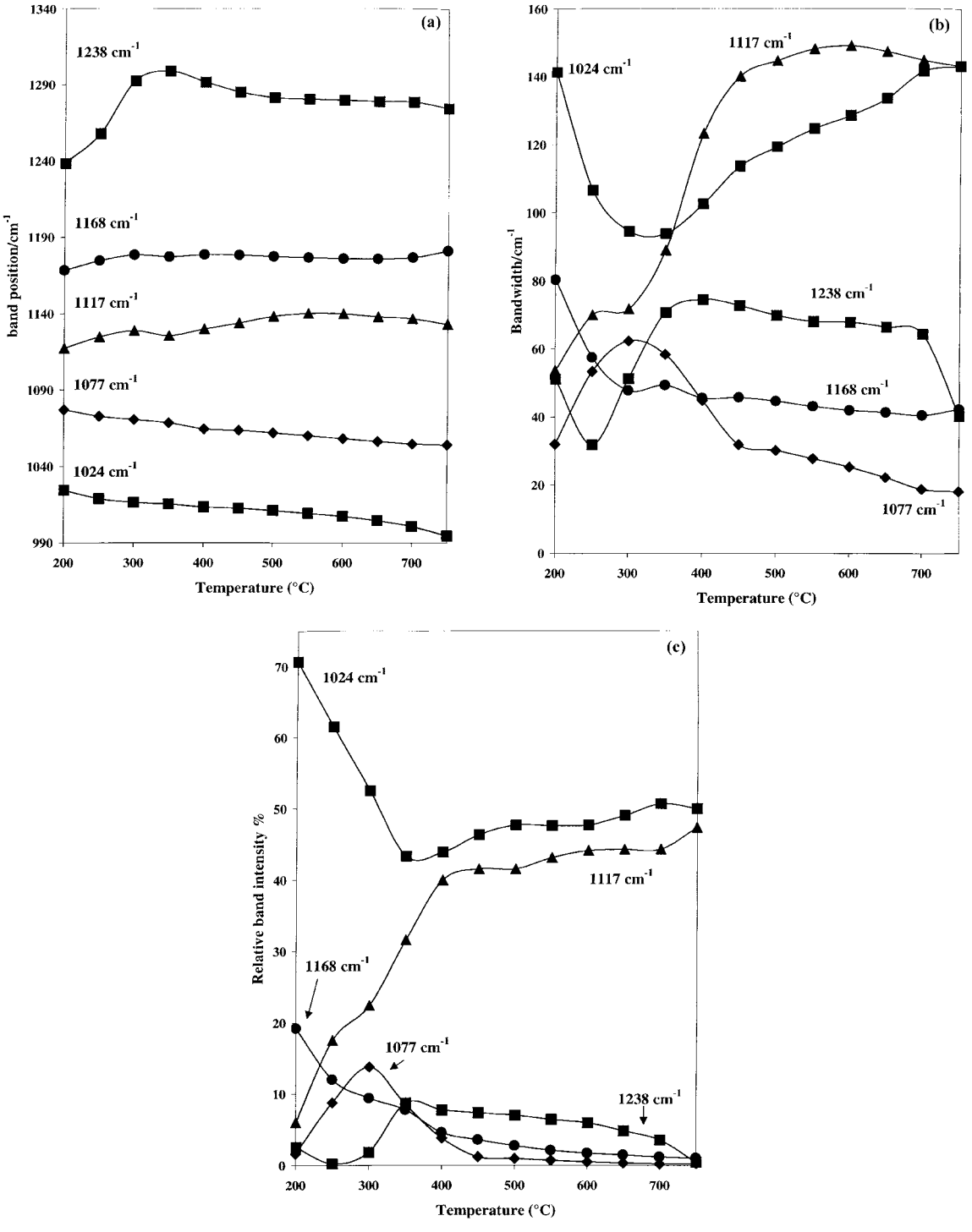

Fig. 5. Changes in the IES (a) band positions, (b) band widths and (c) relative band intensities of the bands in the 1000–1300 cm^{-1} region as functions of the temperature.

diminishes. This is also strongly reflected in the relative band intensities, as functions of temperature, of the 1077 cm^{-1} band.

A very peculiar behavior is shown by the 1238 cm^{-1} band compared to the other bands in this region between 1000 and 1400 cm^{-1}. First, the band shows a strong red shift of more than 50 cm^{-1}, followed by a blue shift above 350°C. The bandwidth reduces to a minimum at 250°C, followed by an increase till 350°C after which it remains nearly constant till 700°C. The relative band intensity shows an opposite behavior. First, it shows an increase till 250°C followed by a decrease till almost zero at 450°C. Based on these observations, we suggest that we are looking at changes not of one band but of two different bands. The first band is the band at 1238 cm^{-1}, which disappears at ≈300–350°C, and a totally new band develops at higher temperatures, which is attributed to a different structure. Calculations on the mass losses observed in the thermogravimetric analysis by Kloprogge et al. [14] have suggested that this must be an anhydrous oxosulfate structure with the general formula of $Al_{26}O_{32}(SO_4)_7$.

Fig. 6 shows the IES spectra of the hydroxyl-stretching region of the basic aluminum sulfate. Although the lower temperature spectra are rather noisy, a very broad band centred on 3300 cm^{-1} and a broad band around 3800 cm^{-1} can be observed. The band around 3300 cm^{-1} resembles the broad band observed for gibbsite ($Al(OH)_3$) [24] and is, therefore, interpreted as the hydroxyl stretching modes of the hydroxyl groups present in the Al octahedra. This band disappears after heating to ≈450°C, which is slightly higher than the 360°C observed in the TGA study [14]. The broad band around 3800 cm^{-1} disappears after heating to 300°C and hass no known interpretation. Based on the position and the disappearance below 350°C, it may be suggested that it must be associated with water or hydroxyl groups in the Al_{13} structure.

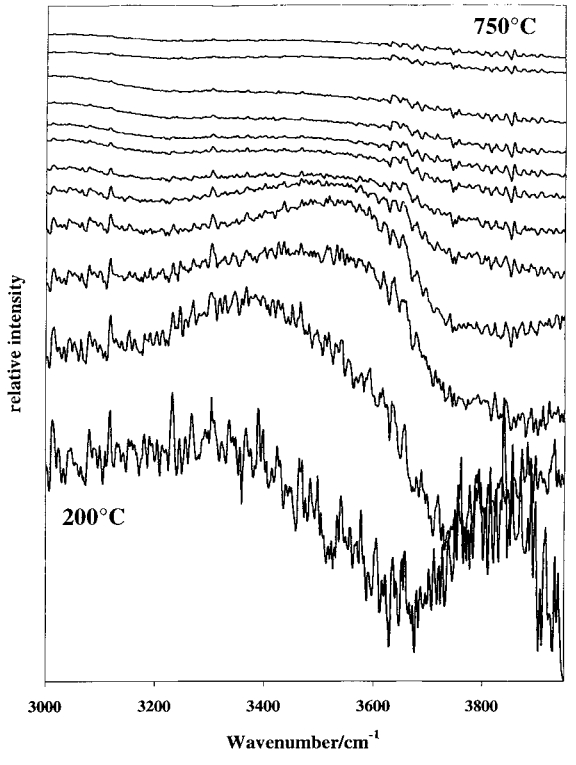

Fig. 6. The infrared emission spectra of basic aluminum sulfate over the 3000–4000 cm^{-1} range and from 200° to 750°C at 50°C intervals.

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