

Thermal decomposition of syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$

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Abstract

The thermal decomposition of syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$, formed during the treatment of liquid manure has been studied by thermal gravimetric analysis, differential scanning calorimetry, high temperature X-ray diffraction (XRD) and infrared emission spectroscopy (IES). Gypsum was found as a minor impurity resulting in a minor weight loss due to dehydration around 100 °C. The main endothermic dehydration and decomposition stage of syngenite to crystalline $K_2Ca_2(SO_4)_3$ and amorphous K_2SO_4 is observed around 200 °C. The reaction involves a solid-state re-crystallisation, while water and the K_2SO_4 diffuse out of the existing lattice. The additional weight loss steps around 250 and 350 °C are probably due to presence of larger syngenite particles, which exhibit slower decomposition due to the slower diffusion of water and K_2SO_4 out of the crystal lattice. A minor endothermic sulphate loss around 450 °C is not due to the decomposition of syngenite or its products or of the gypsum impurity. The origin of this sulphate is not clear.

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1. Introduction

Syngenite was synthesised already in 1850 by J.A. Philips as a by-product during the process of vinegar fermentation [1] but it was not until 1872 that it was discovered as a naturally occurring mineral. Since then, it has been found as one of the crystalline compounds in salt stains on bricks together with gypsum [2,3]. It was also identified by one of the authors of this paper (R.D.S.) as salt stains in the Institute of Earth Sciences, Utrecht University, The Netherlands. Sulphate minerals such as gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($2CaSO_4 \cdot H_2O$), anhydrite ($CaSO_4$) and syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) are also observed in cement [4]. Salem [5] observed the formation of syngenite together with arcanite (K_2SO_4) and gypsum during gaseous corrosion using water vapour and SO_2 gas of K_2O – CaO – SiO_2 glasses.

Dankiewicz and Wieczorek-Ciurowa [6] described the formation of syngenite as an intermediate product in one of the methods developed for the production of mineral fertilisers from naturally occurring polyhalite $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$. The syngenite described in this paper is a product also formed during the production of fertilisers. However, here liquid pig and calf manure is used as the starting material, which is mixed with sulphuric acid to fix the ammonium present in the manure.

Dankiewicz and Wieczorek-Ciurowa [6] also reported on the kinetics of thermal dehydration of their synthetic syngenite under isothermal conditions in the temperature range from 230 to 280 °C. In contrast to these results, Triolo et al. [7] however reported the reaction of syngenite to görgeyite ($K_2Ca_5(SO_4)_6 \cdot H_2O$), arcanite (K_2SO_4) and water around 225 °C. This indicates that the endotherms observed by Nefedow [20] can not be due to the decomposition of syngenite.

The thermal transformation behaviour of minerals and other inorganic compounds like syngenite has only rarely been studied in detail by in situ spectroscopic emission

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methods. The technique of measurement of discrete vibrational frequencies emitted by thermally excited molecules, known as Fourier transform infrared emission spectroscopy (FTIR ES, or shortly IES) [8–10] has only been used to a limited extent for the study of mineral structures (see e.g. [9–18]). The major advantages of IES are that the samples are measured in situ at elevated temperatures and IES requires no sample treatment other than making the sample of sub-micron particle size. Further, the technique removes the difficulties of heating the sample to for example dehydroxylation temperatures and subsequent quenching prior to the measurement, as IES measures the dehydroxylation process as it actually is taking place.

In a recent paper [19], we have described the infrared and Raman spectra of syngenite. C_s site symmetry was determined for the two sulphate groups in syngenite ($P2_1/m$), so all bands are both infrared and Raman active. The split ν_1 modes were observed at 981 and 1000 cm^{-1} . The split ν_2 mode was observed in the Raman spectrum as bands at 424, 441, 471 and 491 cm^{-1} . In the IR spectrum, only one band was observed at 439 cm^{-1} . From the split ν_3 mode, three 298 K Raman bands were observed at 1117, 1138 and 1166 cm^{-1} . Cooling to 77 K resulted in four bands at 1119, 1136, 1144 and 1167 cm^{-1} . In the IR spectrum, five bands were observed at 1110, 1125, 1136, 1148 and 1193 cm^{-1} from the split ν_4 mode, four bands were observed in the IR spectrum at 604, 617, 644 and 657 cm^{-1} . The 298 K Raman spectrum showed one band at 641 cm^{-1} , while at 77 K four bands were observed at 607, 621, 634 and 643 cm^{-1} . Crystal water is observed in the IR spectrum by the OH-liberation mode at 754 cm^{-1} , OH-bending mode at 1631 cm^{-1} , OH-stretching modes at 3248 (symmetric) and 3377 cm^{-1} (anti-symmetric) plus a combination band at 3510 cm^{-1} of the H-bonded OH-mode plus the OH-stretching mode.

This paper aims at determining the thermal decomposition pathway of syngenite using a combination of thermal analysis combined with mass spectrometry of the evolved gases, vibrational spectroscopy (infrared emission spectroscopy) and heating stage X-ray diffraction (XRD) in order to solve the problem raised by the incomplete thermal analysis results published so far [6,7,20].

2. Experimental

2.1. Sample origin

The sample of syngenite was produced as a several millimetre-thick scale in a manure treatment plant at Eibergen, The Netherlands. This plant, owned by agricultural minerals treatment (AMV) treats annually approximately 135,000 tons of liquid pig and calf manure. In order to prevent smell problems, the fresh manure was mixed with sulphuric acid. This strongly reduced the ammonia emission, but adding additional sulphate ions to the system increased

the problem of syngenite formation. After filtration to remove coarse solids, HNO_3 is used to break down H_2S before aeration. After aeration and cleaning the exhaust air, sulphuric acid is mixed with the liquid fraction to fix ammonium, and the acidified mixture is degassed to prevent excessive foam formation. In the next step, the liquid is transferred to a large vacuum vessel. There it flows over a system of pipes, through which boiling water is passed. Thanks to the vacuum, the manure boils already at 60 °C. The heat of condensation is recovered and used to heat the water. In this concentration step of the manure, the solubility product of syngenite is exceeded, resulting in scaling. Fig. 1 shows a characteristic scanning electron microscope (JEOL 35CF scanning EM) image of the syngenite crystals formed. Electron microprobe analysis (JEOL 840A electron probe microanalyser with three wavelength-dispersive spectrometers, a NORAN Be-window Si EDS detector, and a Moran scientific PC-based X-ray microanalysis system) does not reveal the presence of any impurities in the crystals and an overall composition of 53 wt.% SO_4 , 27 wt.% K_2O and 20 wt.% CaO , corresponding to $\text{K}_{1.9}\text{Ca}_{1.05}(\text{SO}_4)_2$. Due to the very high crystal surface roughness, the analyses are not of very high accuracy but do confirm the nature of the syngenite.

For comparison, syngenite was synthesised in the laboratory. Two stock solutions containing the proper amounts of K_2SO_4 and CaSO_4 to obtain the stoichiometric ratio necessary for the synthesis of syngenite were prepared. The K_2SO_4 solution was added to the CaSO_4 solution. After precipitation, the sample was aged at 1 atm in an oil bath for 5 days at 100 °C.

2.2. X-ray diffraction (XRD)

The XRD powder analyses were carried out on a Philips wide angle PW 1050/25 vertical goniometer equipped with a graphite diffracted beam monochromator. The radiation applied was $\text{Cu K}\alpha$. The samples were measured at 50% RH in stepscan mode with steps of 0.02° 2θ from 2.5 to 70° 2θ . High temperature XRD (HT-XRD) data were collected between 30 and 500 °C in stepscan mode with steps of 0.04° 2θ at a scan speed of 1°/min from 9 to 61° 2θ using $\text{Co K}\alpha$ radiation.

2.3. Thermal analysis

The thermal decomposition of the syngenite was carried out in a TA high-resolution thermogravimetric analyser Q500 V2.27 in a flowing nitrogen atmosphere (80 cm^3/min) at a preset, constant decomposition rate of 0.15 mg/min . Below this threshold value the sample was heated under dynamic conditions at a uniform heating rate of 2 °C/min. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stages. The TGA instrument was coupled to a

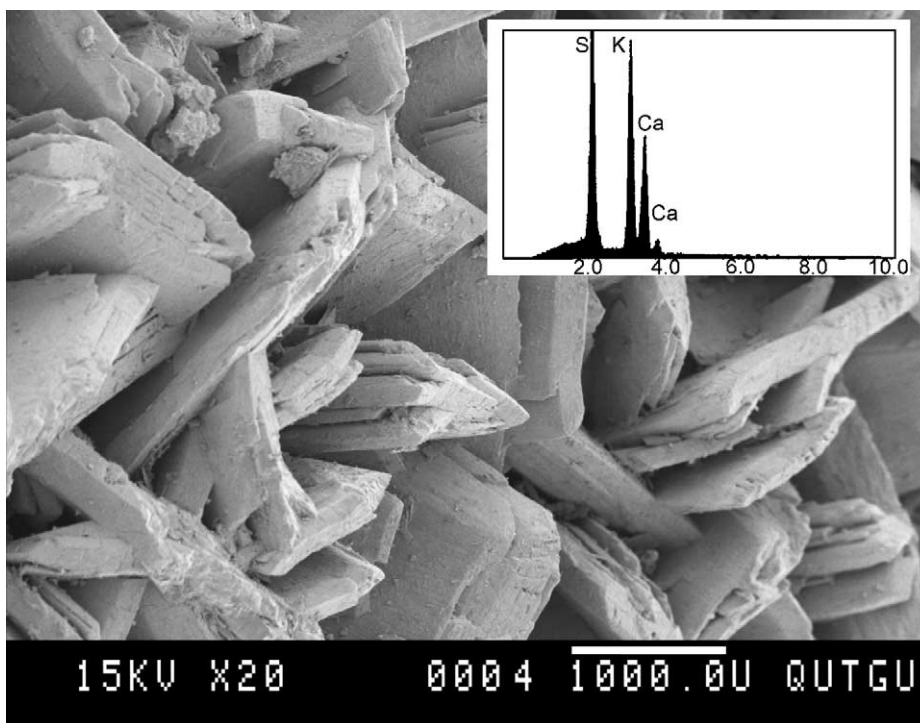


Fig. 1. SEM image of syngenite, inset shows the corresponding EDS analysis.

Balzars (Pfeiffer) Quadstar Series mass spectrometer for gas analysis of water, oxygen and sulphur compounds.

The differential scanning calorimetry (DSC) measurements were carried out in a TA DSC Series Q10 V2.40 and Q100 V6.2 at a constant heating rate of 2 °C/min up to a maximum temperature of 490 °C. In addition, the differential thermal analysis pattern was measured up to 1000 °C and during cooling down till 400 °C in a Seteram simultaneous DTA/TGA instrument operating at a heating rate of 2 °C/min.

2.4. Fourier transform infrared emission spectroscopy (FTIR ES)

FTIR 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 been published elsewhere structures [8–10]. Approximately, 0.2 mg of the sample 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 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 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 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 paraboloidal mirror with a focal length of 25 mm mounted above the heater capturing the infrared radiation and directing 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 paraboloidal mirror. By this means the geometry is such that approximately 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 centre to allow the passage of the laser beam. The mirror was mounted at 45°, which enables the IR radiation to be directed into the FTIR spectrometer. In the normal course of events, three sets of spectra are obtained: (1) the black body radiation over the temperature range selected at the various temperatures, (2) the platinum plate radiation is obtained at the same temperatures and (3) the spectra from the Pt plate covered with the sample. Normally, only one set of black body and Pt radiation is required. The emittance spectrum at a particular temperature was calculated by subtraction of the single beam spectrum of the Pt backplate from that of the Pt + sample, and the result rated to the single beam spectrum of an approximate blackbody (graphite). This spectral manipulation is carried out after all the spectral data have been collected.

The emission spectra were collected at intervals of 50 °C over the range 200–750 °C. The time 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 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} . Good quality spectra can be obtained provided the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret because of self-absorption.

2.5. Heating stage Raman microscopy

Small amounts of the syngenite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with $10\times$, $20\times$ and $50\times$ objectives, for the 300 K measurements. No sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD. Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 500 and 1500 cm^{-1} . Repeated acquisitions using the highest magnification were accumulated to improve the signal-to-noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectra at increased temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, UK). Samples were placed on a circular glass disc, which fitted over the silver plate of the thermal stage. Because of the increased optical path, spectra are noisier and require longer accumulation times. Spectra were obtained using 20 s scans for up to 30 min using the special short $50\times$ (UWLD) objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long-working distance objective. This, combined with the spherical aberration of the stage window, results in a decreased signal compared with that run without the thermal stage.

2.6. Spectral manipulations

Spectral manipulation such as baseline adjustment, smoothing and normalisation of both the IES and Raman spectra were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the software package 'Peakfit' (Jandel, AISN Software Inc.), 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 $r^2 > 0.995$.

2.7. Crystal structure of syngenite

Syngenite has initially been described as a monoclinic mineral with space group $P2_1/m$ by Laskiewicz [21] and Kurylenko [22]. The first report on the crystal structure was, however, based on the space group $P2_1$ on the basis of the positive piezoelectric effect [23]. However, the space group of $P2_1/m$ was later confirmed by the calculations of Corazza and Sabelli [24] and by Nizamutdinov et al. [25]. Their solid-state NMR results showed that the crystal water molecules take up a position of symmetry C_s confirming that the crystal structure must have a plane of symmetry.

The structure of syngenite can be divided in two parts associated with the potassium and the calcium atoms in the unit cell (Fig. 2). The K atoms are surrounded by eight O atoms at the seven corners of a very irregular cube lacking one corner plus one O atom on the centre of one face. The potassium polyhedra, repeated by mirror planes build up a straight chain in the c direction. These chains are then linked together to form a wavy sheet in the c direction parallel to (1 0 0). The Ca atoms are surrounded by nine O atoms. Three of these O atoms lie on the mirror plane, while the other six are symmetrically placed on both sides of the same mirror plane. The Ca polyhedra form a zigzag chain along the c direction, while each Ca polyhedron shares three corners on one side and two corners on the other side with the K polyhedra thereby forming the bridge between the potassium containing sheets. The Ca chains form wavy planes roughly in the bc plane.

The sulphur atoms are present in two special positions with a relatively regular tetrahedral co-ordination. The S_1 tetrahedron shares two oxygen atoms with a Ca polyhedron on one side and two other O atoms with a Ca polyhedron on the other side. The complex of S_1 tetrahedra, with the Ca chains, make up a sheet parallel to (1 0 0). In addition, the S_1 tetrahedra make additional bridges among the K sheets. All of the S_2 tetrahedra share one edge with each of its surrounding K polyhedra and one edge with a Ca polyhedron to form further bonds between the K sheets and the Ca chain [24]. One O atom does not take part in the formation of the two sulphate tetrahedra because it belongs to the crystal water molecule. The water molecule takes part in the polyhedron around the Ca atom but its interaction with the Ca is weak. The protons form a strong hydrogen bond to one of the oxygen atoms surrounding S_2 linked to the Ca atom [26].

The Infrared spectrum will be mainly governed by the sulphate and water modes. Theoretically, when the sulphate retains its full symmetry (T_d) four modes of vibration will be observed: $\nu_1(A_1)$ at 983 cm^{-1} , $\nu_2(E)$ at 450 cm^{-1} , ν_3 at 1105 cm^{-1} and $\nu_4(F_2)$ at 611 cm^{-1} . The A_1 (symmetric stretching) and E (bending) modes are Raman active only, while the F_2 stretching and bending modes are both Raman and infrared active. The crystal structure data reveal that only two S–O bonds are identical in each sulphate group leading to a point group of C_s . In addition, it is shown that the two sulphate groups, although having the same point group, are not identical as the bond lengths and angles are different and

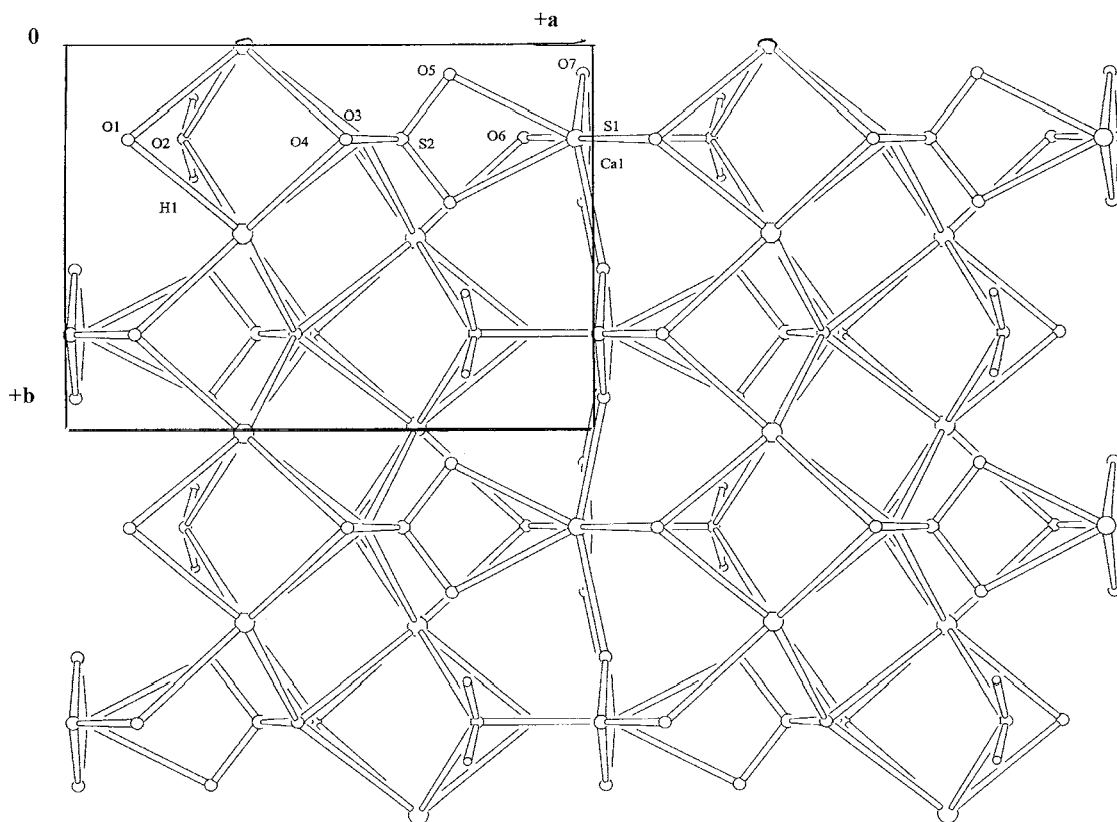


Fig. 2. Projection of the syngenite crystal structure along the *c*-axis.

the oxygen atoms are bonded to different cations. Therefore, two times nine active bands are expected in both the Raman and infrared spectra. The crystal water molecule will be present in the form of OH-stretching, bending and translation modes around roughly 3000–4000, 1600 and 750 cm^{-1} .

3. Results

Fig. 3 shows the XRD patterns of the syngenite formed in the manure treatment plant and the synthetic syngenite. Minor amounts of impurities could be identified in the

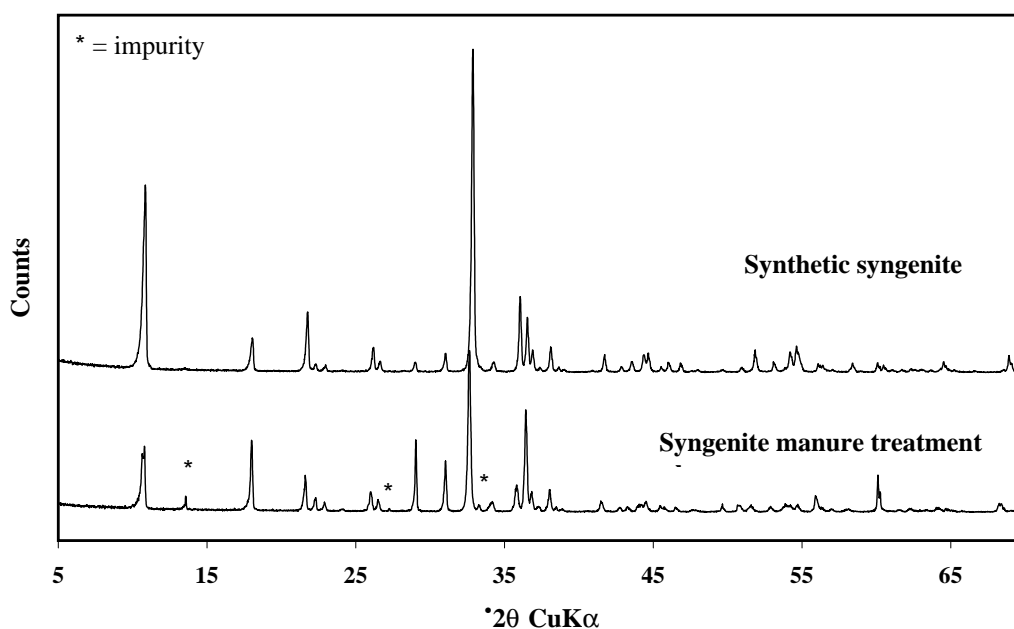


Fig. 3. XRD patterns of the syngenite formed in the manure treatment plant and the synthetic syngenite.

Table 1
TGA–MS and DSC analysis of the syngenite from the manure treatment plant

Step	Onset weight loss (°C)	Endpoint weight loss (°C)	DSC endothermic peak temperature (°C)	MS peak temperature (°C)	TGA weight loss (%)	Theoretical weight loss (%)	Evolved gas
1	80	125	122	101	0.50	0.5	H ₂ O
2	170	200	227	195	6.50	5.5	H ₂ O
3	200	225	258	228	0.23		H ₂ O, SO ₂ , SO
3a	225	280	–	250	1.27		H ₂ O
4	280	365	315	325	0.30		H ₂ O, SO, SO ₂
4a	365	450	365	420	4.17		SO, SO ₂
5	450	530	461	495	0.19		SO ₂ , SO

syngenite from the manure treatment plant as being gypsum and ammonium nitrate.

The thermogravimetric curve (TG) and the corresponding differential thermogravimetric curve (DTG) are shown in Fig. 4a and 5a, while the DSC curve is shown in Fig. 4b. The evolution of various gasses as a function of temperature is represented in Fig. 4c and 5b. The corresponding weight losses are summarised in Table 1. The first endothermic weight loss of 0.50% between 80 and 125 °C is caused by the loss of only water. The mass spectrum, however, shows a minor release of water around 55 °C, which corresponds with the slightly sloping start of the TGA curve before Step 1. The second endothermic weight loss of 6.50% between 170 and 200 °C represents the largest loss observed for syngenite and is again only due to the release of water. The third endothermic weight loss of 1.50% is observed between 225 and 275 °C and is due to the loss of water plus small amounts of SO and SO₂. The mass spectra indicate the loss of all three compounds around 227 °C (0.23 wt.%) followed by only the loss of SO and SO₂ around 250 °C (1.27 wt.%). Step 4 also concerns the loss of 0.30% water, SO and SO₂ around 325 °C (Step 4) and around roughly 420 °C, 4.17 wt.% SO and SO₂ (Step 4a), followed by Step 5 where a small amount of 0.19% of SO₂ and SO is lost up to 530 °C. The corresponding DSC, however, shows only one endotherm for Step 3, while the three endotherms corresponding to Steps 4, 4a and 5 are observed at slightly lower temperatures around 315, 365 and 461 °C.

Fig. 6 shows the results of heating the syngenite in situ in the HT-XRD up to 500 °C. The room temperature pattern reveals a minor amount of gypsum as an impurity next to the syngenite. The gypsum pattern is hardly visible in the 50 °C pattern and has completely disappeared in the 100 °C pattern. Up to 200 °C no changes are observed in the diffraction pattern of the syngenite. Associated with the major weight loss observed in the TG experiment around Steps 2 and 3, a major structural change is observed at 240 °C. The newly formed phase has been identified as K₂Ca₂(SO₄)₃, although a minor amount of syngenite is still present. Another minor change is observed from 400 to 450 °C, which is probably associated with Steps 4 and 5 in the TG experiment and the complete disappearance of the syngenite.

Fig. 7 shows the infrared emission spectra of the syngenite between 100 and 450 °C. The spectrum at 100 °C is identical

to earlier-published IR spectra of syngenite [19]. The split ν_1 can be observed at 981 and 1000 cm⁻¹. The split ν_2 (theoretical four infrared bands) observed as only a single band around 439 cm⁻¹ in the infrared absorption spectrum could not be observed in the IES spectra due to the detection limit at 550 cm⁻¹. From the split ν_3 (theoretical six infrared bands) five bands were observed at 1110, 1125, 1136, 1148 and 1193 cm⁻¹ in the infrared absorption spectrum [19]. Due to the broadness of the IES bands these bands are all overlapping resulting in one broad band. From the split ν_4 (theoretical six infrared) four bands were observed at 604,

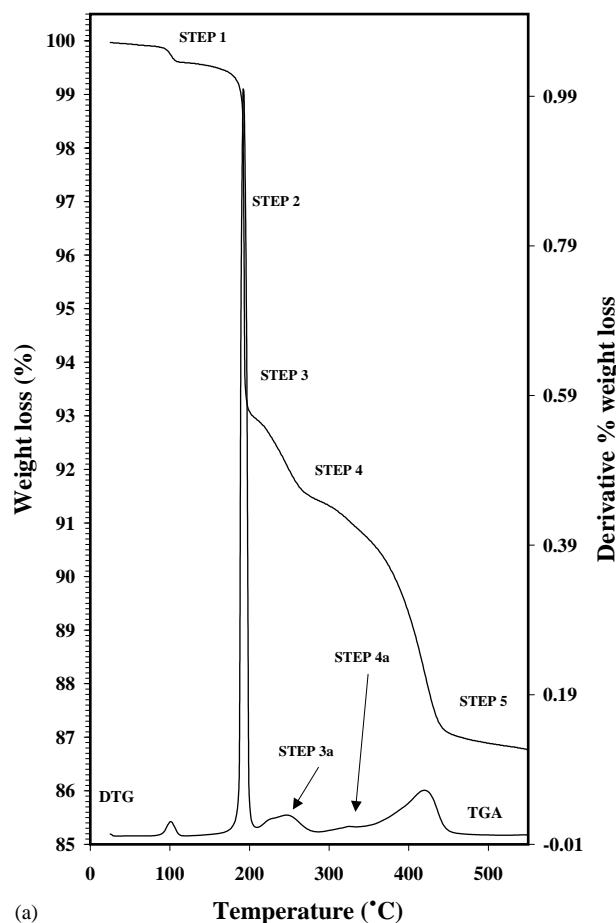
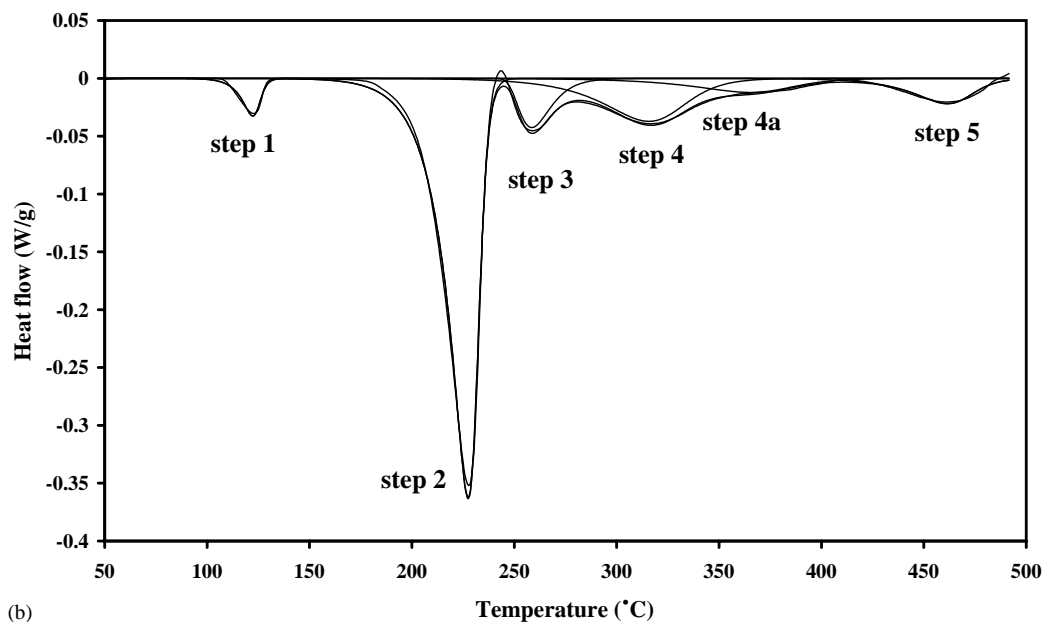
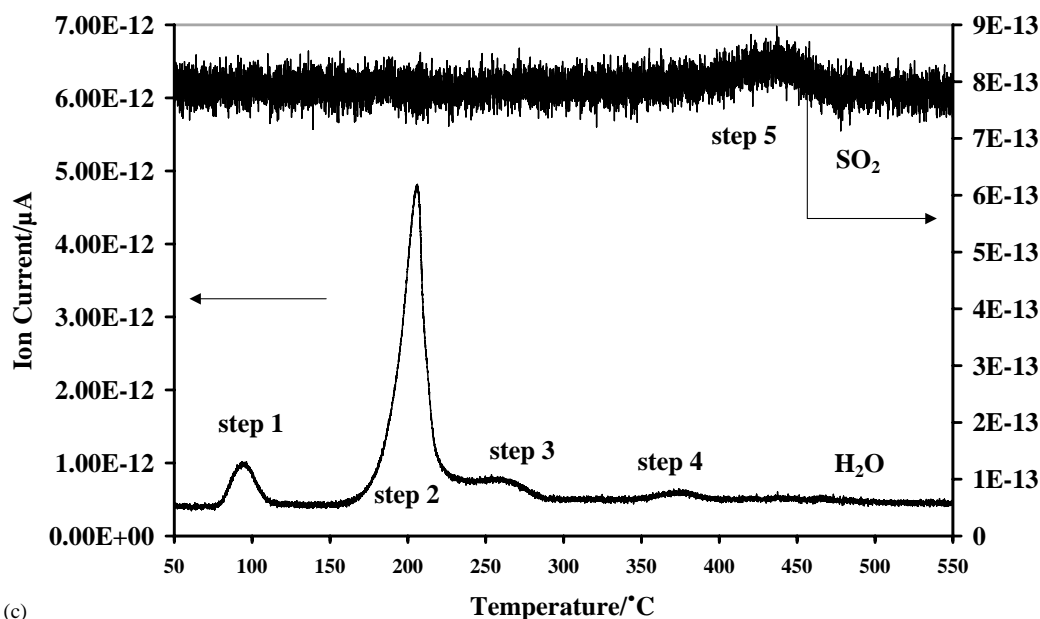


Fig. 4. (a) TGA plot, (b) DSC plot and (c) corresponding mass spectrometry plot of syngenite from manure treatment plant.



(b)



(c)

Fig. 4. (Continued).

617, 644 and 657 cm^{-1} . Crystal water is observed in the infrared spectrum by the OH-libration mode at 754 cm^{-1} , OH-bending mode at 1631 cm^{-1} , OH-stretching modes at 3248 (symmetric) and 3377 cm^{-1} (anti-symmetric) plus a combination band at 3510 cm^{-1} of the H-bonded OH-mode plus the OH-stretching mode.

During heating to 200 °C, no drastic changes are observed in the low wavenumber regions of the spectra except a decrease in intensity. However, a very strong decrease is observed in the OH-stretching region between 2500 and 4000 cm^{-1} plus the associated OH-bending mode at 1631 cm^{-1} and liberation mode at 754 cm^{-1} , indicating the

almost complete disappearance of water from the system. The spectrum at 225 °C differs strongly from the spectrum at 200 °C, which agrees well with the strong weight loss Step 2 observed in the TGA and the phase change revealed in the heating stage XRD patterns. The newly formed $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ is characterised by a sulphate ν_1 mode at 978 cm^{-1} , a split ν_3 mode around 1105, 1169 and 1245 cm^{-1} and a split ν_4 mode around 617, 627, 639 and 663 cm^{-1} .

The minor amount of water still visible as a very weak OH-stretching band disappears around 375–400 °C, which is consistent with the TGA–MS, which shows no further

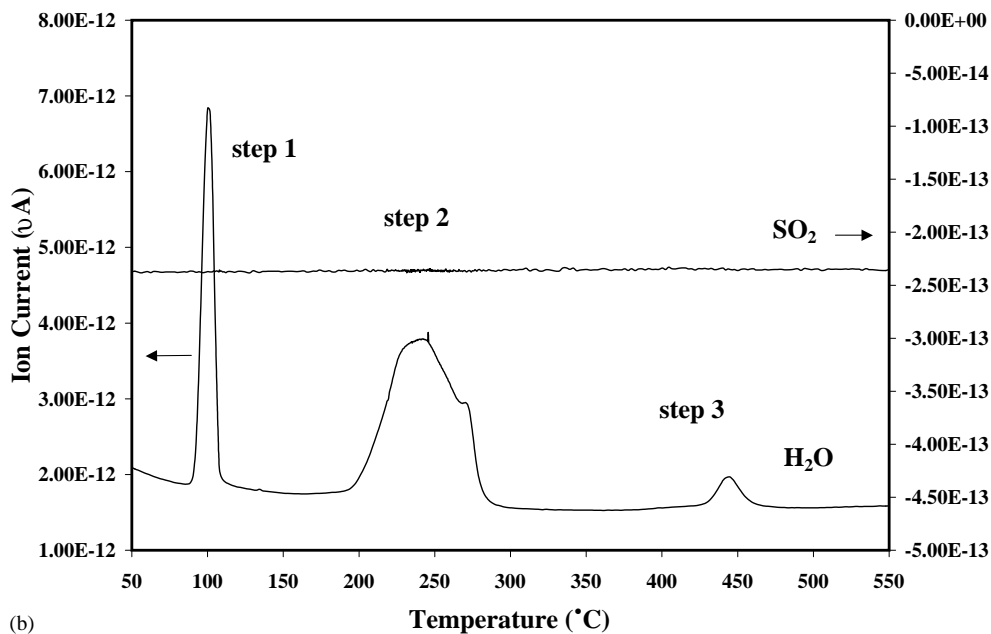
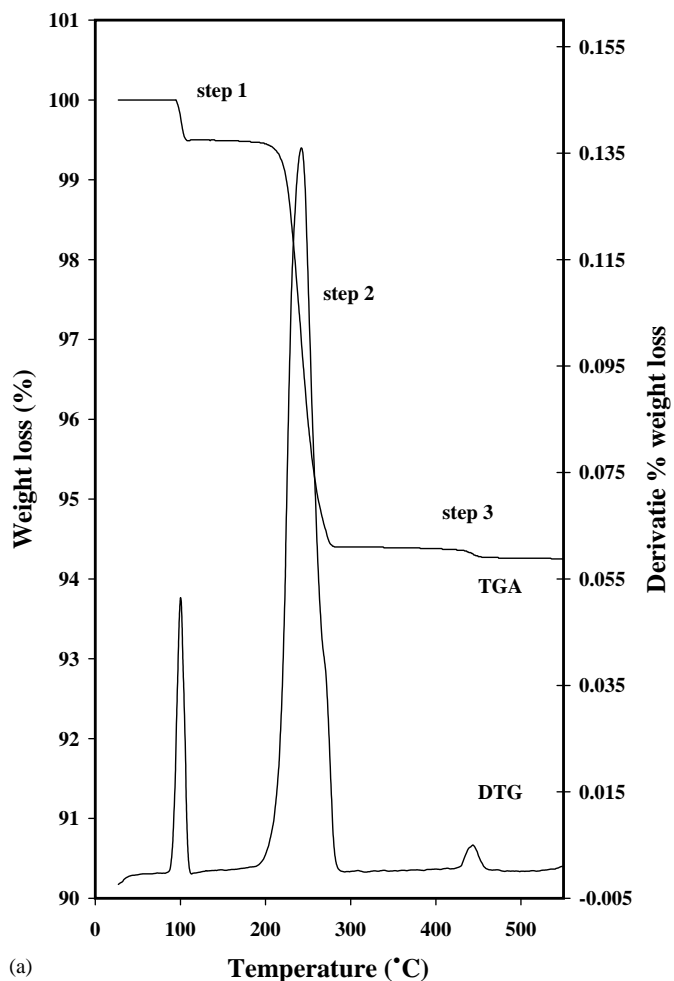


Fig. 5. (a) TGA plot and (b) corresponding mass spectrometry plot of synthetic syngenite.

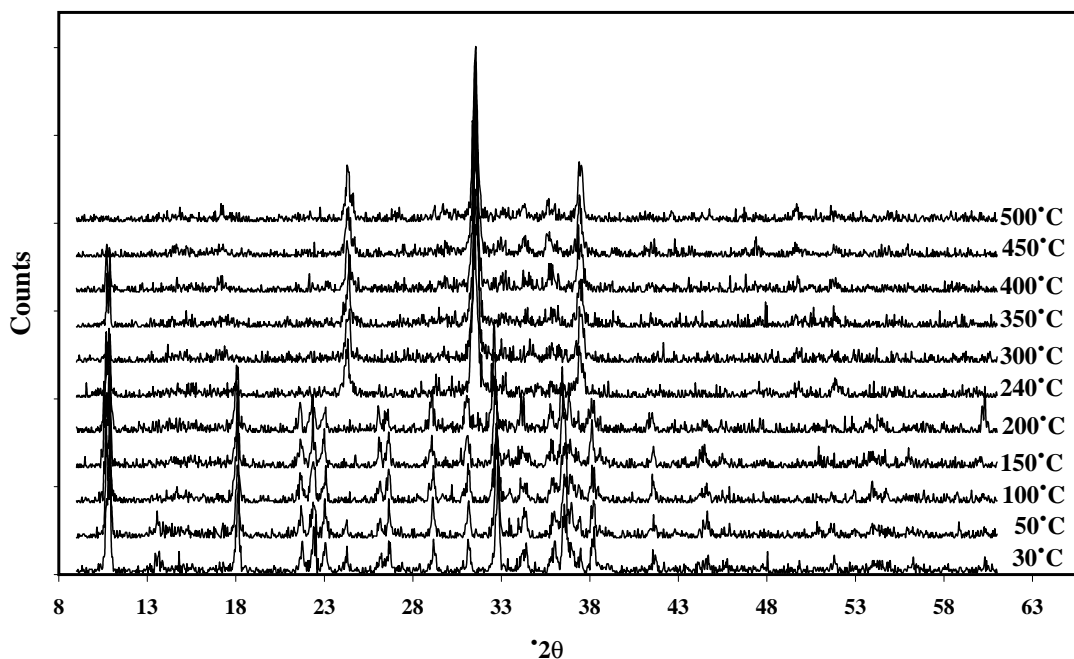


Fig. 6. HT-XRD patterns of syngenite between 30 and 500 °C.

loss of water after to 375 °C. In the temperature range from 225 to 450 °C, no further major changes are observed but minor changes do occur due to the thermal expansion of the material.

The heating stage Raman spectra (Fig. 8) shows a pattern similar to that of the IES spectra. Up to 175 °C, the region between 900 and 1200 cm^{-1} is dominated by two strong bands at 981 and 1003 cm^{-1} associated with the ν_1 mode of the sulphate group. At 200 °C, these two bands are only recognisable as a single shoulder around 981 cm^{-1} while the other band is hidden under a new band at 993 cm^{-1} . Heating to 225 °C results in the formation of another band at 1017 cm^{-1} . Upon further heating the 993 cm^{-1} band disappears again and above 250 °C a band appears at 978 cm^{-1} . The two weak bands around 1150 cm^{-1} ascribed to the corresponding ν_3 mode disappear after heating above 175 °C.

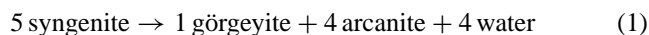
A similar pattern is observed in the low wavenumber region between 400 and 550 cm^{-1} . Here, the bands associated with the sulphate ν_2 mode at 427, 441, 473 and 493 cm^{-1} disappear after heating to 200 °C, where it is replaced by a new band at 445 cm^{-1} with a shoulder at 453 cm^{-1} . Upon further heating the 453 cm^{-1} band becomes more intense, while the 445 cm^{-1} band disappears.

4. Discussion

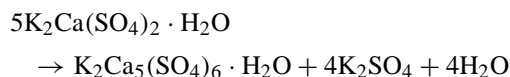
In the interpretation of TGA curves of minerals and other inorganic compounds the small loss of water around 55 °C and the first endothermic weight loss between 80 and 125 °C is in most cases ascribed to adsorbed water. However, in

this specific case the weight loss is also due to the two dehydration steps of the gypsum via metastable bassanite (or hemihydrate) $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ to $\gamma\text{-CaSO}_4$. The amounts of bassanite and $\gamma\text{-CaSO}_4$, however, are too small to be observed in the XRD patterns. The observed weight loss for the first stage of dehydration indicates the presence of maximally 3 wt.% gypsum in the sample.

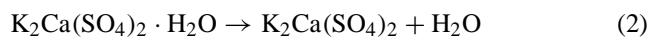
The temperature interval from 170 to 200 °C and the corresponding DSC peak at 227 °C agree closely with the temperature of 225 °C reported by Triolo et al. [7] for the re-crystallisation of syngenite to görgeyite and arcanite according to the following reaction:



or



The loss of water in this reaction would result in a theoretical weight loss of 4.4%, which is significantly less than the observed 6.5%. Based on the data from the HT-XRD and the IES, the following dehydration reaction seems the most logical alternative:



This dehydration reaction would result in a theoretical weight loss of 5.5%, which is close to the observed weight loss. Dankiewicz and Wieczorek-Ciurowa [6] studied the thermal behaviour of syngenite because it was formed as an intermediate product in one of the methods developed

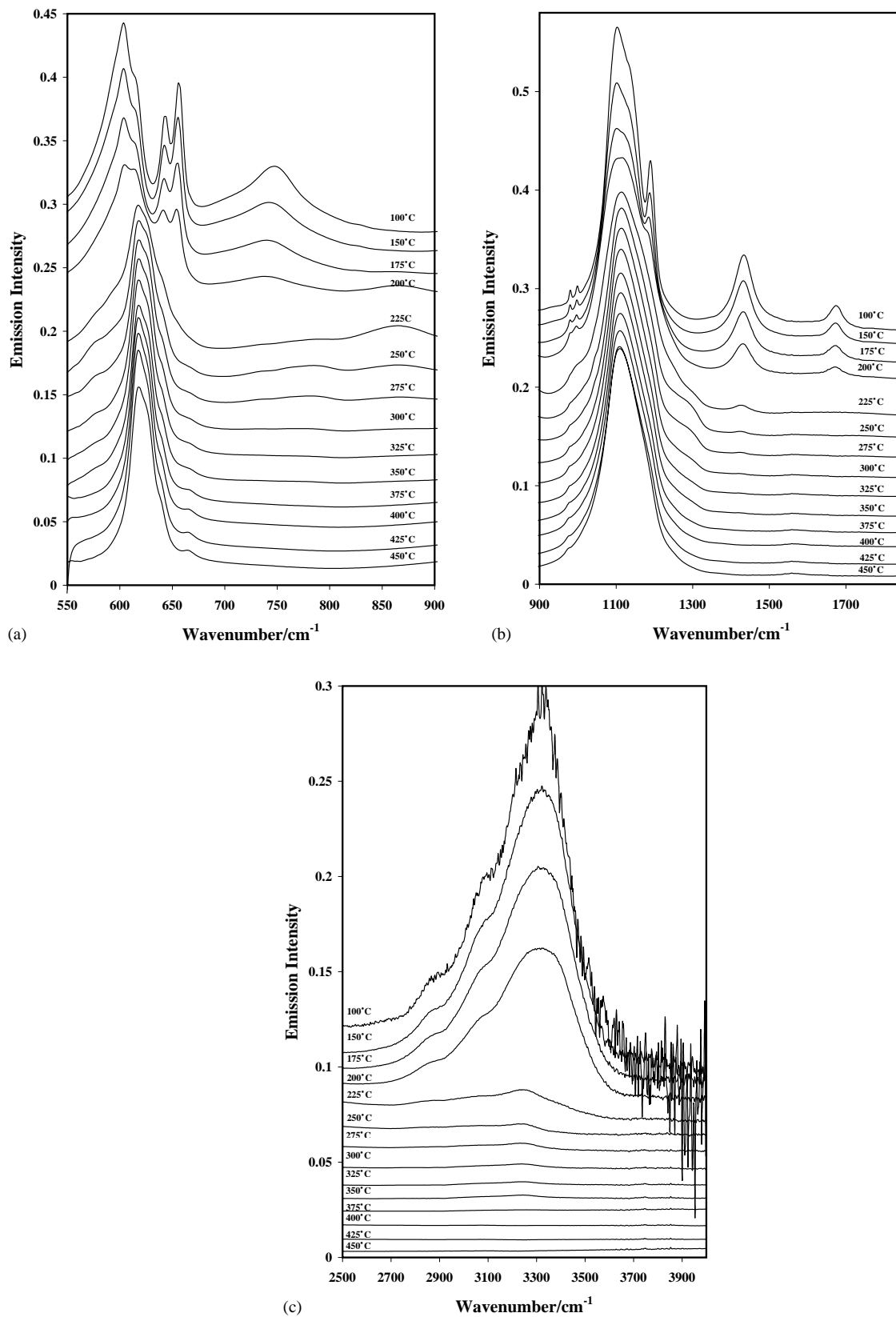


Fig. 7. IES patterns of syngenite in the regions between (a) 550 and 900 cm⁻¹, (b) 900 and 1800 cm⁻¹ and (c) 2500 and 4000 cm⁻¹.

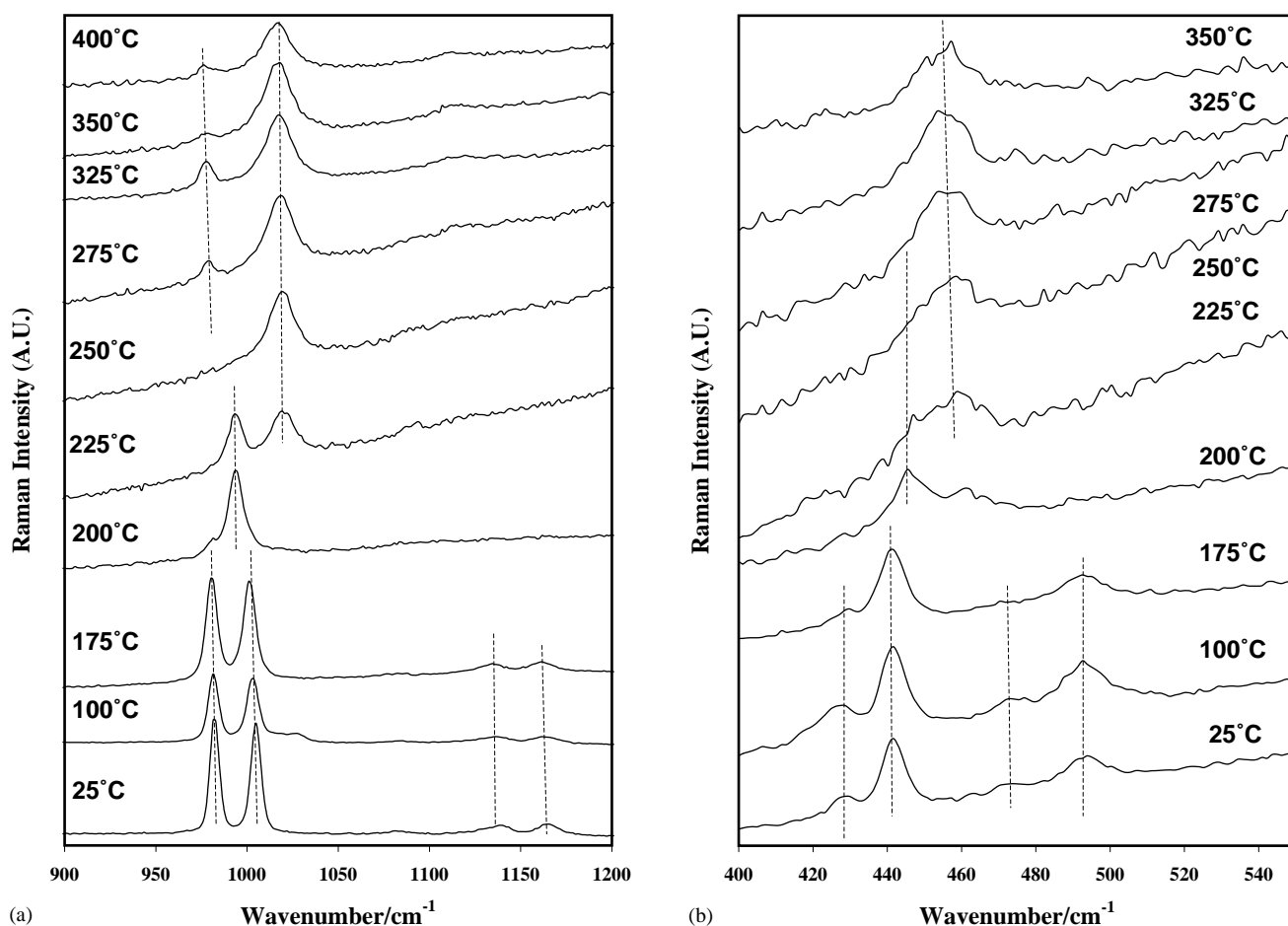
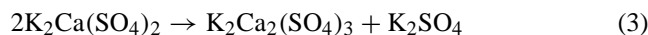


Fig. 8. Heating stage Raman spectra in the regions between (a) 900 and 1200 cm^{-1} and (b) 400 and 550 cm^{-1} .

for the production of mineral fertilisers from naturally occurring polyhalite $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. They concluded from their experiments in a static air atmosphere under isothermal conditions that dehydration takes place between 230 and 280 °C. They concluded that this dehydration reaction follows a single mechanism corresponding to the random nucleation Avrami Eq. (1) where $Kt = [-\ln(1 - \alpha)]^{1/2}$ with α the degree of decomposition, t the time and K the rate constant. They calculated an activation energy of 342.2 ± 15.5 kJ/mol. The HT-XRD, however, in contrast to the interpretation of Dankiewicz and Wiczorek-Ciurowa [6], indicates the formation of $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ instead at 240 °C as the only crystalline component according to the reaction:



This reaction does not involve any weight losses either and will, therefore, not be observed in the TGA. The DSC pattern does not reveal an extra endotherm around this temperature, which indicates that both reactions [2,3] are taking place simultaneously.

The heating stage Raman spectra indicate the formation of an intermediate product before crystallisation of the

$\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ takes place. The IES also indicate the presence of an intermediate although it is not as clearly visible as in the Raman spectra. Broad bands around 1300, 875, 775 and 725 cm^{-1} in the 200–250 °C spectra are probably associated with this phase. This intermediate phase could not be observed in the HT-XRD.

During the heating of the syngenite from room temperature to about 150 °C, where the onset of the dehydration/decomposition is observed in the TGA and DSC, strong thermal expansion of 0.0022 $\text{\AA}/^\circ\text{C}$ along the a -axis can be observed plus much smaller thermal expansions for the b - and c -axis of 0.0001 and 0.0002 $\text{\AA}/^\circ\text{C}$, respectively (Fig. 9). As soon as the dehydration/decomposition starts, the crystal structure starts to collapse along the a -axis, while the expansion along the other two axes continues. The diffusion of water during this reaction has to take place along the bc plane, while at the same time the K_2SO_4 is separated from the remaining lattice structure re-organising itself to $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$.

The HT-XRD shows that a minor amount of the syngenite survives up to 400 °C, while the IES spectra exhibit a weak OH-stretching mode around 3250 cm^{-1} visible up to 375 °C. This can explain the minor water loss of Step 3a in the

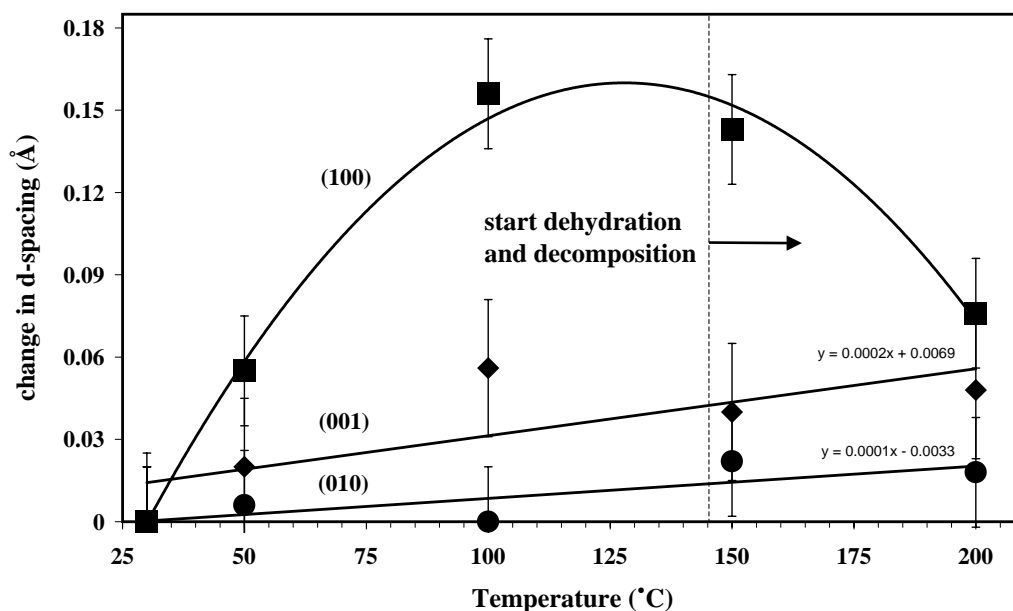


Fig. 9. Change in thermal expansion along the three crystallographic axes of syngenite as function of temperature.

TGA. This is associated with the presence of large crystals where the diffusion of water is hindered, resulting in higher dehydration temperatures.

Further evidence for this interpretation is given by the TGA–MS of the synthetic syngenite, which does not show a separate Step 3 but a broadened Step 2 over a wider temperature range. Steps 4 and 4a associated with the loss of water are not observed in the TGA–MS of the synthetic syngenite, indicating that these two steps are probably due to other impurities in the syngenite sample from the manure treatment plant.

The last weight loss (Step 5), associated with a minor endotherm in the DSC does not result in any changes in the HT-XRD patterns or in the IES spectra. The mass spectra indicate a minor loss of H₂O, SO₂ and SO, which are breakdown products in the spectrometer of SO₃. The exact nature of this de-sulphurisation reaction is unclear as both CaSO₄ and K₂SO₄ decompose at much higher temperatures than 450 °C. The release of the sulphate is probably due to a small amount of excess sulphuric acid not identified by any of the analytical techniques. In the same temperature range, the synthetic syngenite (Step 3) also show a small weight loss, although much smaller than for the sample from the treatment plant and only associated with the loss of H₂O and not of any sulphate compounds. This is in agreement of the assumption that a small amount of sulphuric acid can be the cause for the weight loss observed for the syngenite from the manure treatment plant. The origin of the small amount of water in the synthetic syngenite sample is unclear though.

In conclusion, it can be said that syngenite dehydrates and decomposes simultaneously around 200 °C to form crystalline K₂Ca₂(SO₄)₃ and amorphous K₂SO₄. This in contrast to earlier work by Dankiewicz and Wiczczyk-Ciurowa

[6], who only reported the dehydration of syngenite. The K₂Ca₂(SO₄)₃ is most probably formed by solid-state re-crystallisation, while the water and K₂SO₄ diffuses out of the decomposing syngenite crystals.

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