JOURNAL OF MATERIALS SCIENCE **34** (1999) 4367 – 4374

# Raman microscopy study of basic aluminum sulfate

## Part II *Raman microscopy at 77 K*

J. T. KLOPROGGE*, R. L. FROST
*Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Q 4001, Australia*
*E-mail: t.kloprogge@qut.edu.au*

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 crystallised as the monoclinic basic aluminum sulfate $Na_{0.1}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}$. These crystals have been studied using Raman microscopy at 300 and 77 K and compared to $Na_2SO_4{\cdot}xH_2O$ and $Al_2(SO_4)_3{\cdot}xH_2O$. The Raman spectrum of basic aluminum sulfate is dominated by two broad bands, which are assigned to the $\nu_2$ and $\nu_4SO_4^{2-}$ triplets at 446, 459 and 496 cm$^{-1}$ and 572, 614 and 630 cm$^{-1}$. The $\nu_1$ is observed as a single band at 990 cm$^{-1}$, partly overlapped by the $\nu_3$ triplet at 979, 1009 and 1053 cm$^{-1}$ of the sulfate group in the $Al_{13}$ sulfate structure. Furthermore the band at 726 cm$^{-1}$ is assigned to an Al–O mode of the polymerised Al–O–Al bonds in the $Al_{13}$ Keggin structure. For the first time the OH-stretching region of the basic aluminum sulfate has been reported. The 77 K spectrum shows the presence of 3 crystal water bands at 3035, 3138 and 3256 cm$^{-1}$ accompanied by 3 Al–$H_2O$ bands at 3354, 3418 and 3498 cm$^{-1}$ and 4 Al-OH bands at 3533, 3584, 3671 and 3697 cm$^{-1}$.

## 1. Introduction

Aluminum is known to form large variety of complexes in solution upon hydrolysis. One of these complexes is a Keggin type structure known as $Al_{13}$ or as the tridecameric complex $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ [1–3]. This complex can be formed by forced hydrolysis of $Al^{3+}$ solutions by the addition of a basic solution like sodium hydroxide or carbonate. The structure of this complex was first studied by X-ray diffraction after precipitation in the form of two different basic aluminum sulfates in which the $Al_{13}$ structure is retained [4–7].

Kloprogge *et al.* [8, 9] described the precipitation of monoclinic basic aluminum sulfate $Na_{0.1}[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_{3.55} \cdot 9H_2O$.$^{27}$Al Solid-state Magic-Angle Spinning Nuclear Magnetic Resonance spectroscopy showed that the tridecameric was preserved in the crystal structure. The infrared spectrum of basic aluminum sulfate is dominated by two strong water peaks at 3247 and 1640 cm$^{-1}$, a strong Al-OH stretching band at 3440 cm$^{-1}$ and sulfate bands at 1135, 980, 715, 610, 566, and 450 cm$^{-1}$ together with some minor bands of incorporated nitrate [8, 10, 11]. In two recent papers the Raman spectrum of basic aluminum sulfate has been reported [12, 13]. The Raman spectrum of basic aluminum sulfate is dominated by two broad bands which were assigned to the $\nu_1$ and $\nu_3$ bands at 981 and 1051 cm$^{-1}$ of the sulfate group in the $Al_{13}$ sulfate structure. Furthermore the band at 724 cm$^{-1}$ was assigned to an Al–O mode of the polymerised Al–O–Al bonds in the $Al_{13}$ Keggin structure. The sharp band at 1066 cm$^{-1}$ and the minor band at 1384 cm$^{-1}$ were interpreted to be due to a small amount of nitrate impurity on a different position in the structure than the nitrate present in the $Al_{13}$ nitrate crystal structure, based on the shift in band position of both the $\nu_1$ symmetric stretching and $\nu_3$ antisymmetric stretching modes.

This paper forms part two of our study of the Raman spectroscopy of basic aluminum sulfate. In this paper the Raman spectra obtained at room temperature are compared to spectra obtained at liquid nitrogen temperature (77 K). Cooling a sample to 77 K is known to result in an increased resolution due to the fact that bands become sharper. Furthermore, in some cases molecules become located in more fixed positions [14–16].

These effects can be of great help in the interpretation and assignment of Raman bands in complex spectra, especially when bands are overlapping and band component analysis does not give a definite answer. Therefore, the aim of this paper is to study the Raman spectrum of basic aluminum sulfate in order to come to a more detailed assignment of the various Raman active modes.

---

* Author to whom all correspondence should be addressed.

## 2. Experimental

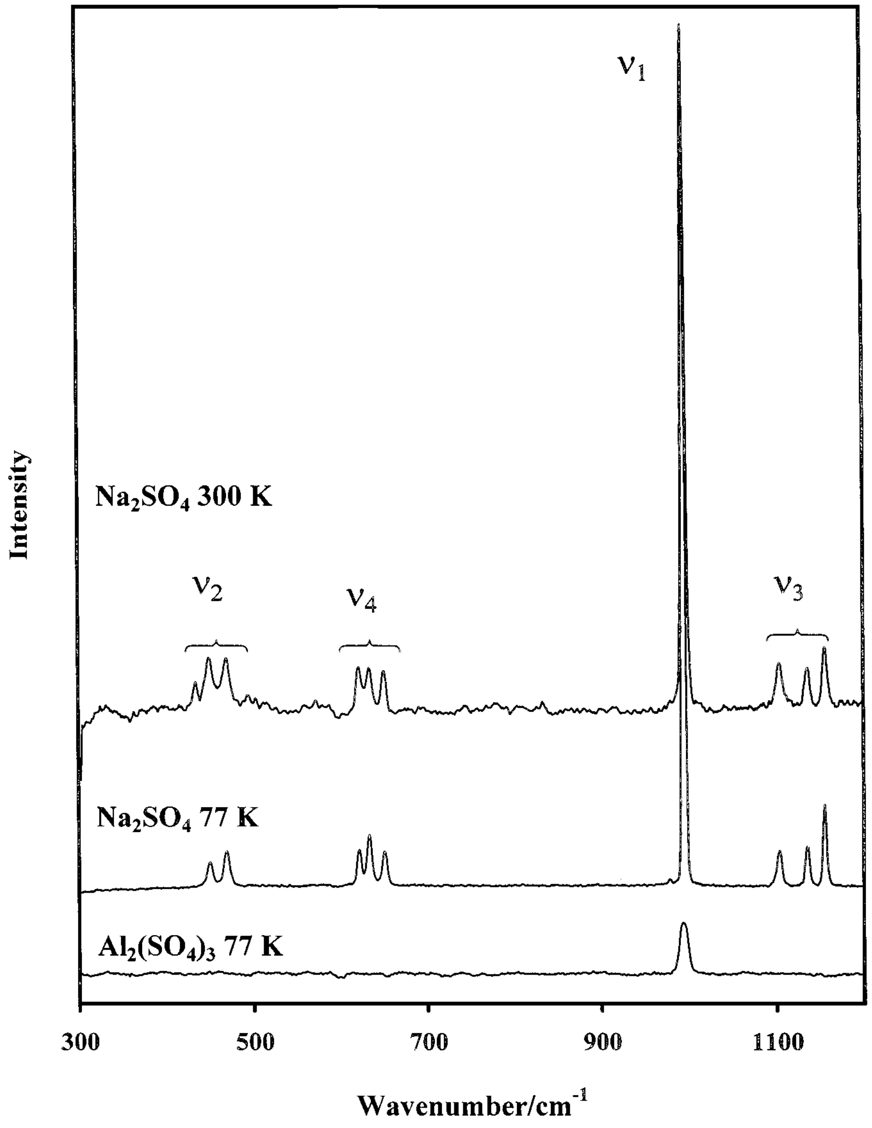
### 2.1. Basic aluminum sulfate

The synthesis and characterisation of the monoclinic basic aluminum sulfate used in this study has been extensively described by Kloprogge *et al.* [2, 8, 9, 11, 12]. 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 50 days before removal from the solution. Crystals collected from the wall of the container were shown to be phase pure [8].

### 2.2. Raman microprobe spectroscopy

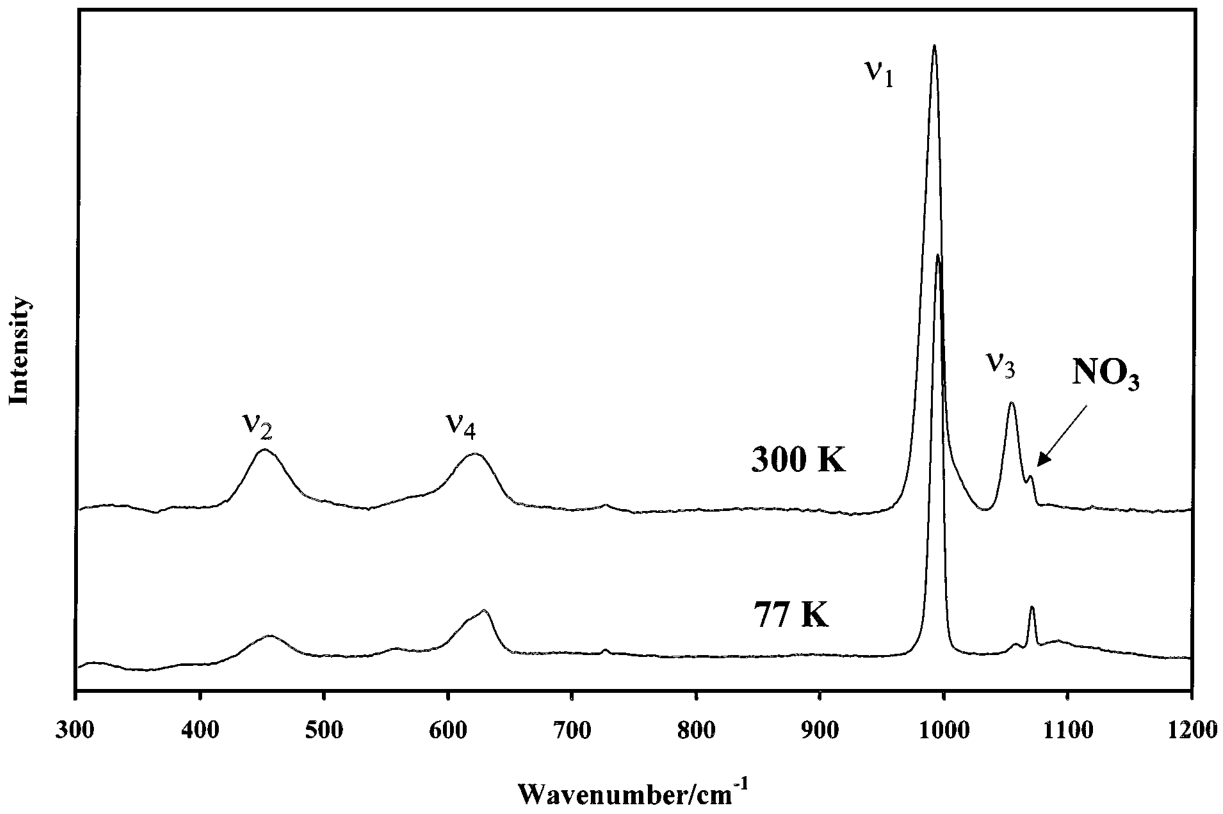
Small amounts of the basic aluminum sulfate were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10*x*, 20*x*, and 50*x* objectives, for the 300 K measurements. No sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope 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 acquisition 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 low temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd., Waterfield, Surrey, England). Samples were placed in three metal cups on a circular glass disc, which fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. Because of the increased optical path, spectra at 77 K are noisier and require longer accumulation times. Spectra were obtained using 20 s scans for up to 30 min using the special short 50X (ULWD) objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this



(a)

*Figure 1* Raman spectra at 300 and 77 K of $Na_2SO_4$ and $Al_2(SO_4)_3$ (a) and basic aluminum sulfate at 300 and 77 K (b) in the region between 300 and 1200 $cm^{-1}$. (*Continued*).



(b)

*Figure 1* (*Continued*).

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.

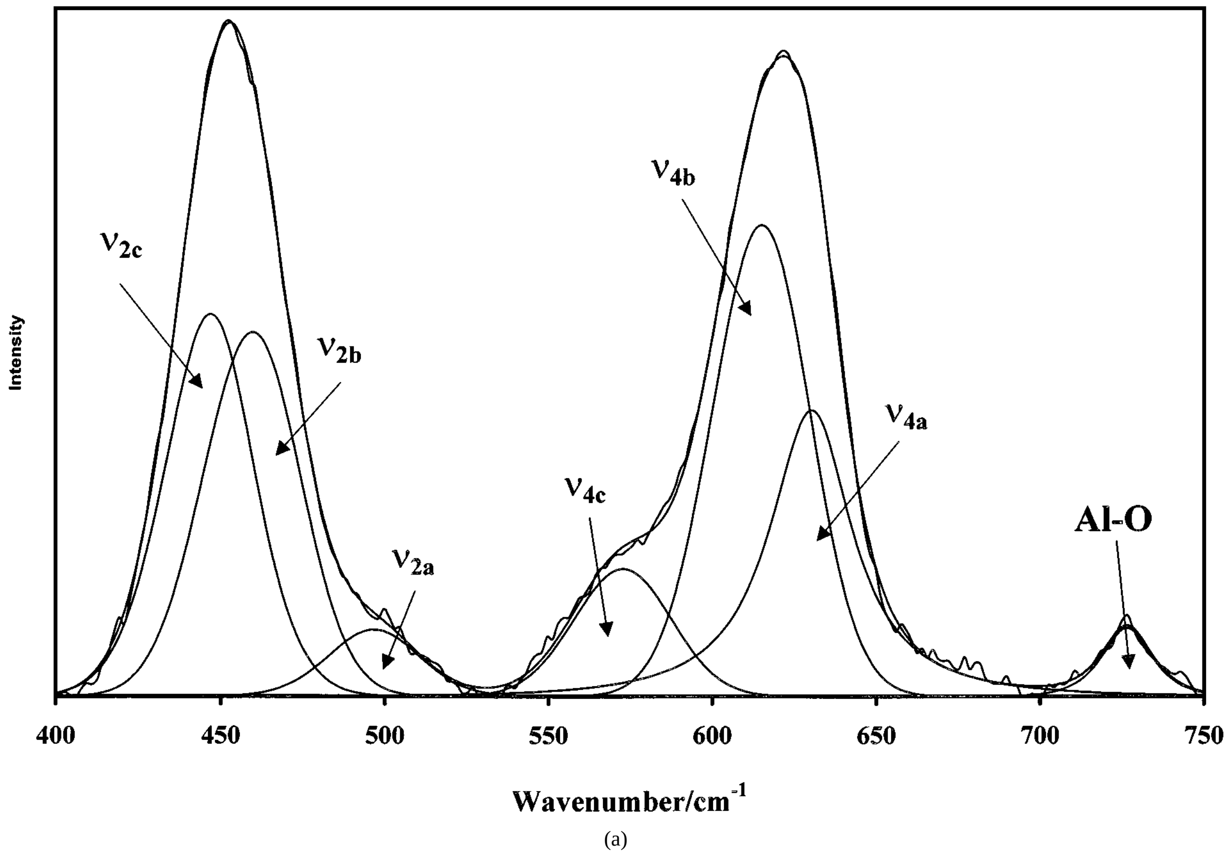
Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function 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 greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2$ greater than 0.995.

## 3. Results and discussion

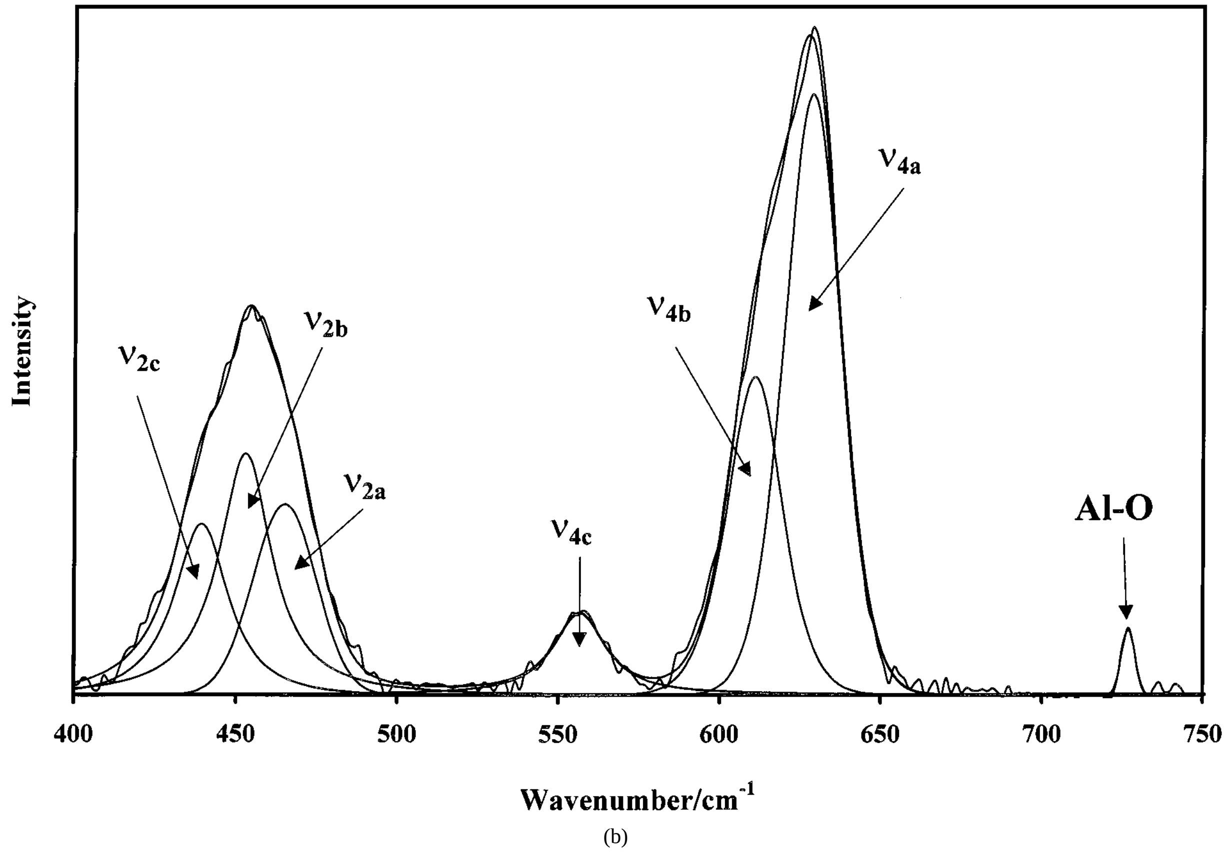
Fig. 1a depicts the Raman spectra of sodium and aluminum sulfate in comparison to the basic aluminum sulfate at 300 and 77 K (Fig. 1b). The use of a new lens of better optical quality has resulted in an increased quality of the spectra. For example the Raman spectrum of sodium sulfate now clearly shows the three triplets associated with the $\nu_2$, $\nu_3$ and $\nu_4$ of the $SO_4$ group [17, 18] compared to the spectra reported in our previous paper [13]. Cooling to 77 K resulted in a decrease in linewidth and the disappearance of one of the $\nu_2$ bands. Also the spectra at 300 and 77 K of the basic aluminum sulfate shows an increased resolution compared to our previous study [13]. The low frequency region shows two broad bands around approximately 450 and 625 $cm^{-1}$. Band component analysis of the Raman spectra at 300 and 77 K (Fig. 2 and Table I) reveals that these signals are actually two strongly overlapping

TABLE I Band component analysis of the Raman spectra at 300 and 77 K of basic aluminum sulfate, $Na_2SO_4 \cdot xH_2O$ and $Al_2(SO_4)_3 \cdot xH_2O$ in the region between 300 and 1200 $cm^{-1}$

| Sample | Band position, $cm^{-1}$ (300 K) | Band position, $cm^{-1}$ (77 K) | Suggested assignment [17, 18] |
|---|---|---|---|
| $Al_{13}$ sulfate | 446 | 439 | |
| | 459 | 453 | $\nu_2SO_4$ triplet |
| | 496 | 465 | |
| | 572 | 557 | |
| | 614 | 611 | $\nu_4SO_4$ triplet |
| | 630 | 628 | |
| | 726 | 727 | Al–O |
| | 979 | 980 | $\nu_3SO_4$ |
| | 990 | 992 | $\nu_1SO_4$ |
| | 1009 | | $\nu_3SO_4$ |
| | 1053 | 1058 | $\nu_3SO_4$ |
| | 1069 | 1071 | $\nu_1NO_3$ sym. stretch |
| | | 1097 vb | Not known |
| $Al_2(SO_4)_3 \cdot xH_2O$ | 991 | 994 | $\nu_1SO_4$ |
| $Na_2SO_4 \cdot xH_2O$ | 435 | — | |
| | 449 | 450 | $\nu_2SO_4$ triplet |
| | 470 | 469 | |
| | 621 | 621 | |
| | 633 | 633 | $\nu_4SO_4$ triplet |
| | 650 | 651 | |
| | 992 | 995 | $\nu_1SO_4$ |
| | 1101 | 1104 | |
| | 1131 | 1135 | $\nu_3SO_4$ triplet |
| | 1152 | 1155 | |



(a)



(b)

*Figure 2* Band component analysis of the Raman spectrum at 300 K (a) and 77 K (b) of basic aluminum sulfate in the region between 400 and 750 $cm^{-1}$.

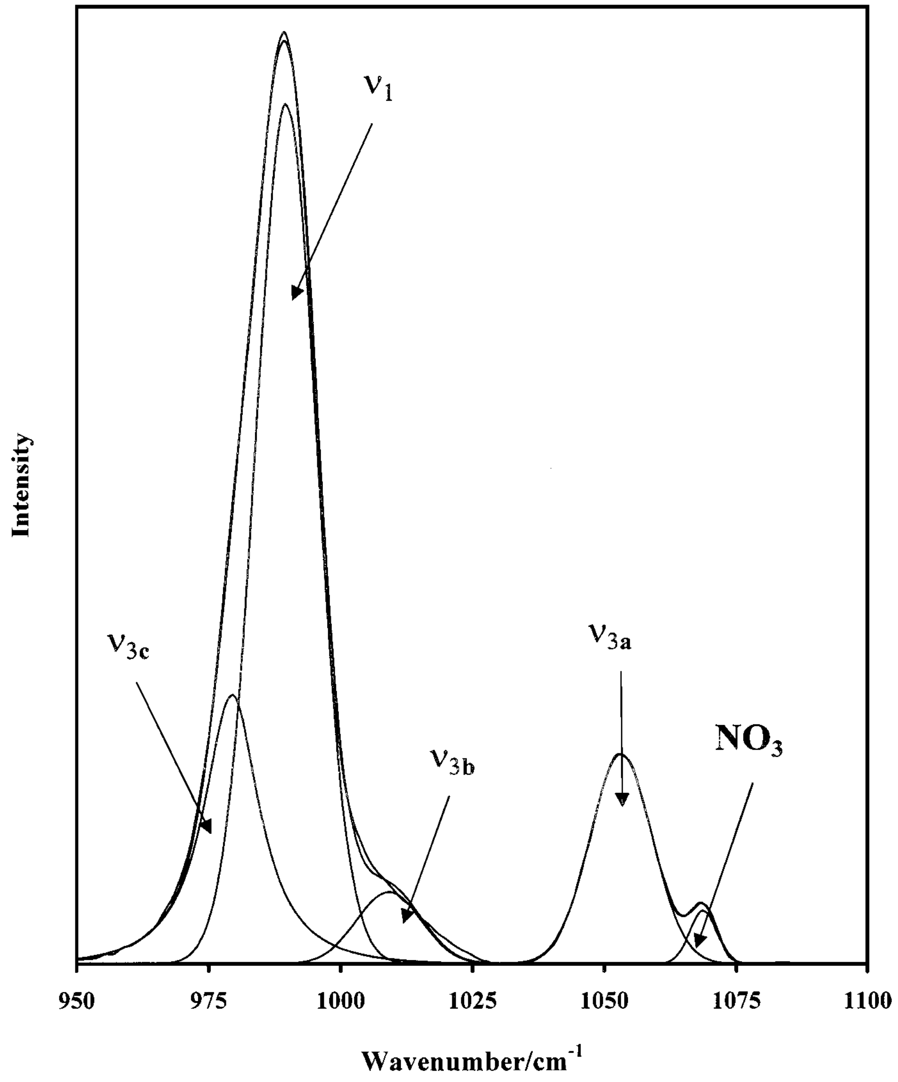
triplets similar to those observed for sodium sulfate. Therefore, these triplets are assigned to the $\nu_2$ and $\nu_4$ of the sulfate groups in the basic aluminum sulfate crystal structure. Again cooling to 77 K results in a decrease in bandwidth and therefore a better resolution especially of the $\nu_4$ triplet. The band previously assigned to Al–O at 726 $cm^{-1}$ show a remarkable decrease in bandwidth from 17.8 to 4.8 $cm^{-1}$.

The precipitation of basic aluminum sulfate from $Al_{13}$ solutions prepared via forced hydrolysis of aluminum nitrate can result in the incorporation of some nitrate in the crystal structure [8, 11, 13]. The crystals used in this study show less nitrate incorporation as evidenced by only a very minor band at 1069 $cm^{-1}$ ($\nu_1$ symmetric stretch) compared to the strong band observed previously at 1066 $cm^{-1}$ [13]. The $\nu_1$ band observed before around 981 $cm^{-1}$ is now found at 990 $cm^{-1}$ accompanied by two overlapping bands on both sides around 979 and 1009 $cm^{-1}$ (Fig. 3a). These two bands together with the band at 1053 $cm^{-1}$ are interpreted to be identical to the $\nu_3$ $SO_4$ triplet observed for sodium sulfate, although distributed over a wider frequency range. This interpretation is supported by the fact that upon cooling to 77 K all three bands strongly diminish in intensity whereas the $\nu_1$ remains strongly present (Fig. 3b).

Fig. 4 shows the hydroxyl-stretching region of the Raman spectrum at 300 K of basic aluminum sulfate. The broad bands in this region have not been observed before [13]. At 300 K a very broad band is found between approximately 2800 and 3800 $cm^{-1}$ with a minor shoulder visible around 3700 $cm^{-1}$. Cooling to 77 K greatly enhances the resolution in this region with the emergence of a broad shoulder around 3150 $cm^{-1}$ and three bands around 3525, 3575 and 3700 $cm^{-1}$. Table II reports the band component analysis of this region, which is also shown in Fig. 5. Clearly six bands with similar bandwidth can be identified and four bands

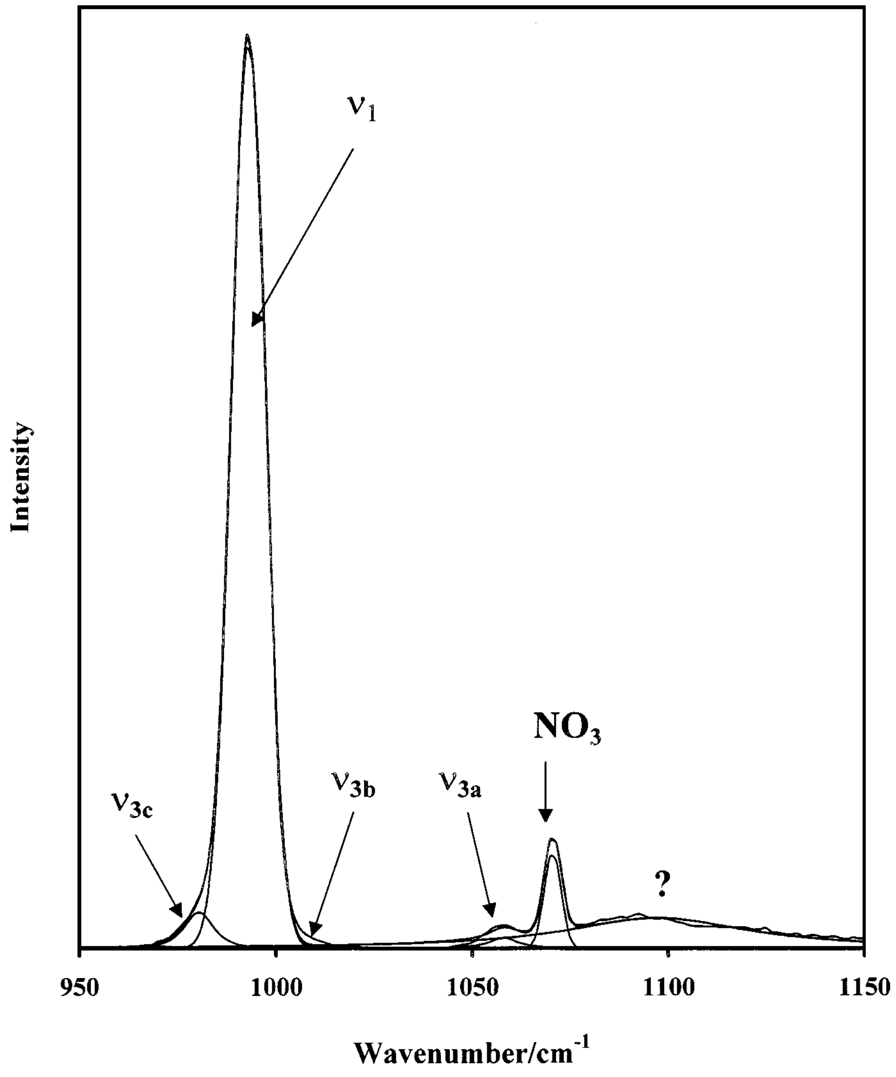
TABLE II Band component analysis of the hydroxyl-stretching region of the Raman spectrum at 77 K of basic aluminum sulfate

| Band position ($cm^{-1}$) | Bandwidth ($cm^{-1}$) | Band intensity (%) | Suggested assignment |
|---|---|---|---|
| 3035 | 117 | 4.2 | $H_2O$ |
| 3138 | 125 | 12.9 | $H_2O$ |
| 3256 | 136 | 20.6 | $H_2O$ |
| 3354 | 135 | 22.4 | Al–$H_2O$ |
| 3418 | 123 | 16.6 | Al–$H_2O$ |
| 3498 | 115 | 12.3 | Al–$H_2O$ |
| 3533 | 31 | 0.99 | Al–OH |
| 3584 | 61 | 7.5 | Al–OH |
| 3671 | 49 | 1.4 | Al–OH |
| 3697 | 22 | 1.1 | Al–OH |



(a)

*Figure 3* Band component analysis of the Raman spectrum at 300 K of basic aluminum sulfate in the region between 950 and 1100 $cm^{-1}$ (a) and at 77 K between 950 and 1150 $cm^{-1}$ (b). (*Continued*)



(b)

*Figure 3* (*Continued*).

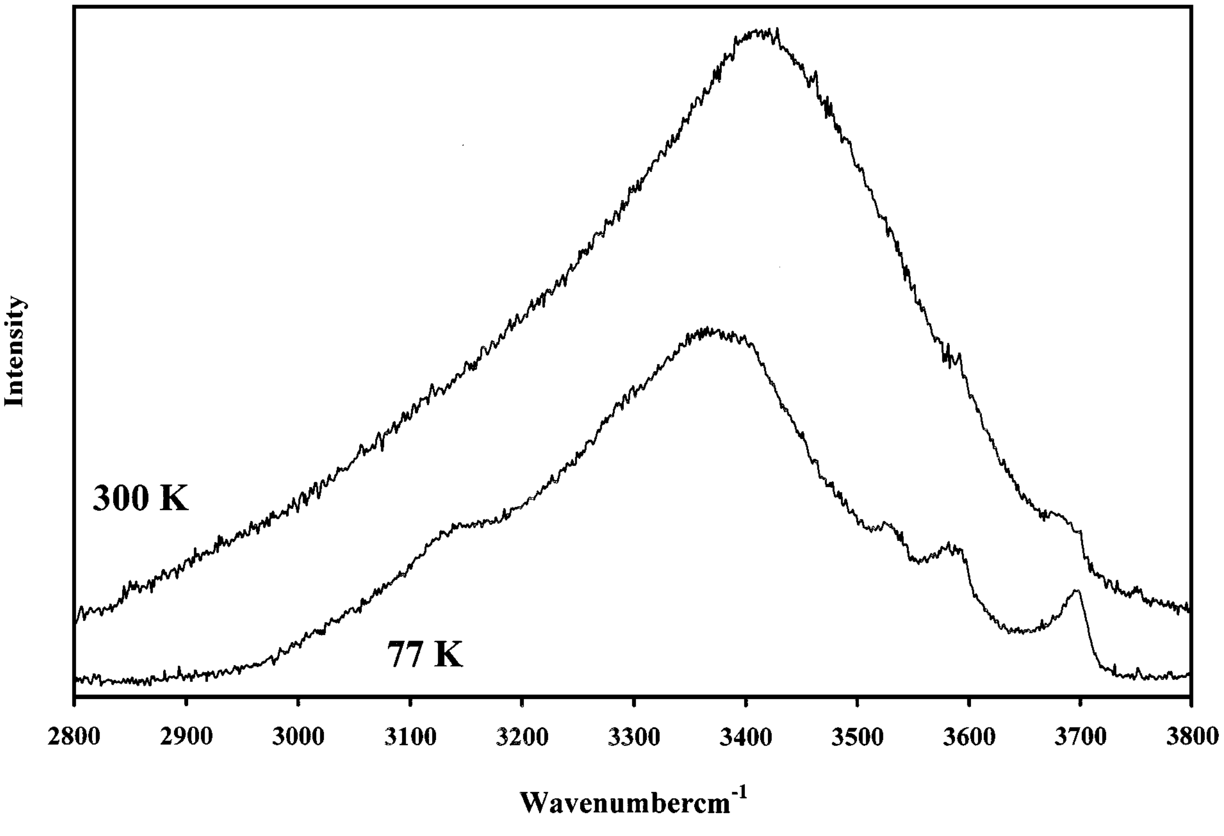


*Figure 4* Raman spectra of basic aluminum sulfate at 300 and 77 K in the hydroxyl-stretching region.

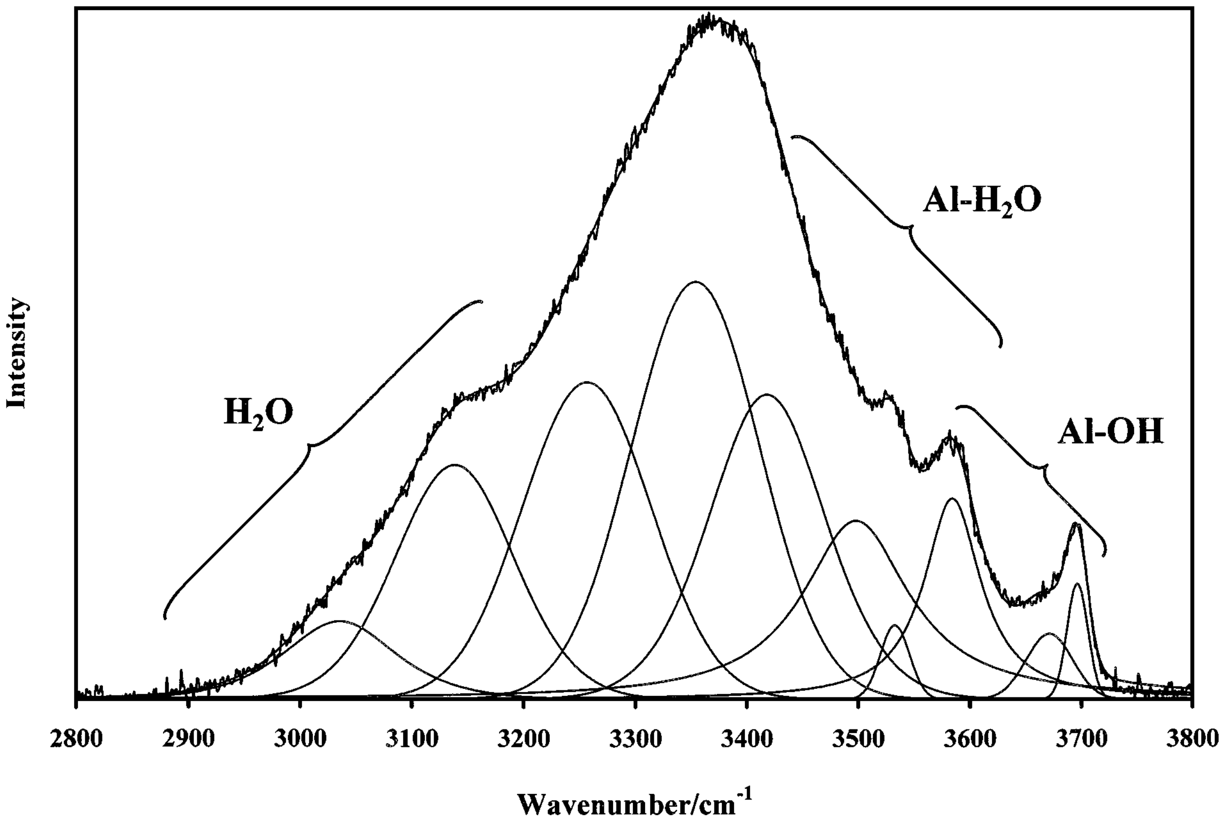


*Figure 5* Band component analysis of the Raman spectrum at 77 K of basic aluminum sulfate in the hydroxyl-stretching region.

at the high frequency side with much narrower bands. Based on the fact that in this region only bands associated with crystal water or Al–H$_2$O and Al–OH from the Al$_{13}$ building unit can be observed, it seems logical to assign the six broad bands to various H$_2$O modes and the other four to Al–OH modes. This agrees with the general observations that water bands are generally observed at lower frequencies and that water bands are generally broader than hydroxyl bands in this region. The first six bands show an average ratio of 1 : 3 : 5 : 5 : 4 : 3. From previous chemical analysis of the basic aluminum sulfate it is known that each unit cell contains 12 water molecules in the Al$_{13}$ building unit and 9 crystal water molecules not associated with the Al$_{13}$ unit [8, 9]. In general, free water molecules are found at lower frequencies than water molecules linked to a cation. Taking this into consideration it is logical to assign the first three bands to the crystal water and the second three bands to Al-H$_2$O, which is also in perfect agreement with the observed ratio of 9 : 12 ($1 + 3 + 5$ and $5 + 4 + 3$).

## 4. Conclusions

Raman spectroscopy of basic aluminum sulfate at 300 and 77 K has shown that, in contrast to earlier publications, the spectra are dominated in the low frequency region by a single $\nu_1$ and three triplets $\nu_2$, $\nu_3$ and $\nu_4$ of the sulfate group together with a single Al–O band around 726 cm$^{-1}$. For the first time the hydroxyl-stretching region of the Raman spectrum of basic aluminum sulfate has been reported. Especially the 77 K spectrum clearly shows the presence of three crystal water bands accompanied by three Al–H$_2$O and four Al-OH bands with increasing frequency. This interpretation has been made possible only because of the increased resolution upon cooling from 300 to 77 K.

## Acknowledgements

The financial and infra-structural support of the Queensland University of Technology, Centre for Instrumental and Developmental Chemistry is gratefully acknowledged. One of us (JTK) is thankful for a QUT postdoctoral fellowship.

## References

1. J. T. KLOPROGGE, D. SEYKENS, J. W. GEUS and J. B. H. JANSEN, *J. Non-Cryst. Solids* **142** (1992) 87.
2. J. T. KLOPROGGE, D. SEYKENS, J. B. H. JANSEN and J. W. GEUS, *ibid.* **142** (1992) 94.
3. R. J. M. J. VOGELS, PhD thesis, Utrecht University, The Netherlands, 1996, chap. 7, p. 157.
4. G. JOHANSSON, *Acta Chem. Scand.* **14** (1960) 771.
5. *Idem., ibid.* **16** (1962) 403.
6. *Idem., Ark. Kemi* **20** (1963) 321.
7. G. JOHANSSON, G. LUNDGREN, L. G. SILLÉN and R. SÖDERQUIST, *Acta Chem. Scand.* **14** (1960) 769.
8. J. T. KLOPROGGE, J. W. GEUS, J. B. H. JANSEN and D. SEYKENS, *Thermochimica Acta* **209** (1992) 265.
9. J. T. KLOPROGGE, P. J. DIRKEN, J. B. H. JANSEN and J. W. GEUS, *J. Non-Crystal. Solids* **181** (1995) 151.
10. D. L. TEAGARDEN, J. F. KOZLOWSKI and J. L. WHITE, *J. Pharm. Sci.* **70** (1981) 758.
11. J. T. KLOPROGGE and R. L. FROST, *Thermochimica Acta* **320** (1998) 245.
12. J. T. KLOPROGGE, R. L. FROST and R. FRY, in Proc. 16th Int. Conf. Raman Spectrosc, Cape Town, South Africa, September 6–11, 1998, edited by A. M. Heyns (1998) p. 700.

13. J. T. KLOPROGGE and R. L. FROST, *J. Mater. Sci* (1999) in press.
14. U. JOHANSSON, R. L. FROST, W. FORSLING and J. T. KLOPROGGE, *Appl. Spectrosc.* **52** (1998) 1277.
15. R. L. FROST, W. FORSLING, A. HOLMGREN, J. T. KLOPROGGE and J. KRISTOF, *J. Raman Spectrosc.* **29** (1998) 1065.
16. R. L. FROST, J. KRISTOF, E. HORVATH and J. T. KLOPROGGE, *Clays Clay Miner.* (1999), 1988 submitted.
17. S. D. ROSS, "Inorganic Infrared and Raman Spectra" (McGraw-Hill, London, 1972) p. 414.
18. J. R. FERRARO, "Low Frequency Vibrations of Inorganic and Coordination Compounds" (Plenum Press, New York, 1971) p. 265.

*Received 13 February*
*and accepted 23 February 1999*