

Raman microscopy study of basic aluminum sulfate

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The tridecameric aluminum polymer $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ 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 $\text{Na}_{0.1}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_{3.55}$. These crystals have been studied using FT-Raman microscopy and compared to the basic aluminum nitrate, $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$. The Raman spectrum of basic aluminum sulfate is dominated by two broad bands which are assigned to the ν_1 and ν_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} is 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} are 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 ν_1 symmetric stretching and ν_3 asymmetric stretching modes.

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1. Introduction

Forced hydrolysis of Al^{3+} solutions by the addition of a base like sodium carbonate or sodium hydroxide or homogeneous hydrolysis by the decomposition of urea is known to result in the formation of large aluminum (oxo)hydroxide complexes. One of these complexes is the tridecameric complex or Al_{13} , $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ [1–3]. This tridecamer can be visualised as a central tetrahedral AlO_4 surrounded by 12 $\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2$ octahedrals in the form of a cage. Besides the use of this polymer in the preparation of pillared clay 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 [9].

Johansson and coworkers [10–13] 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 crystallised in the cubic system whereas the sodium-free sulfate crystallised in the monoclinic system.

In a more recent paper Kloprogge *et al.* [14, 15] described the precipitation of monoclinic basic aluminum sulfate with a small amount of sodium and a trace of nitrate. Based on their chemical analyses by ICP-AES they reported a chemical composition per unit cell of $\text{Na}_{0.1}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_{3.55} \cdot 9\text{H}_2\text{O}$. ^{27}Al Solid-state Magic-Angle Spinning Nuclear Magnetic

Resonance spectroscopy showed that the tridecameric units were still present in the crystal structure.

Kloprogge *et al.* [14] and Teagarden *et al.* [9] have briefly described the infrared spectrum of basic aluminum sulfate. The 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} . Kloprogge *et al.* [14] also observed some minor peaks of incorporated nitrate in the infrared spectra of his original crystals. These bands disappeared after washing. These infrared data were recently confirmed by Infrared Emission Spectroscopy, which also showed minor nitrate bands [16].

To date there is only one brief report on the Raman spectroscopy of basic aluminum sulfate [17]. The objective of this research is to extensively report the FT-Raman spectrum of basic aluminum sulfate and to compare them to basic aluminum nitrate, hydrated sodium- and aluminum sulfate in order to get more insight in the structure of this complex aluminum salt.

2. Experimental

2.1. Basic aluminum sulfate and nitrate

The synthesis and characterisation of the monoclinic basic aluminum sulfate used in this study has been extensively described by Kloprogge *et al.* [2, 14–17]. The tridecameric aluminum polymer was obtained by forced hydrolysis of a 0.5M aluminum nitrate solution

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with a 0.5M 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 0.5M 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. The basic aluminum nitrate was prepared from the same hydrolysed aluminum solution followed by very slow evaporation of the excess water at room temperature.

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 \times , 20 \times , and 50 \times objectives. 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. 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. 1b depicts the Raman spectrum of the basic aluminum sulfate. This spectrum is characterised by two broad bands at 981 and 1051 cm⁻¹ and a sharp band at 1066 cm⁻¹. Based on the position and broadness of the 981 cm⁻¹ band compared to a similar band in the Al₂(SO₄)₃·xH₂O and Na₂SO₄·xH₂O spectra (Fig. 1a and d respectively), this band is assigned to the ν_1 of the SO₄ group in the basic aluminum sulfate group. Based on the broadness of the band at 1051 cm⁻¹ this band is also assigned to the sulfate group in the basic aluminum sulfate. Comparison with the Na₂SO₄·xH₂O spectrum leads to the conclusion that this must be the single ν_3 band instead of the triplet observed in other sulfates like sodium or barium sulfate [18, 19]. This means that the sulfate group has lost its degeneracy and has become less distorted as can be expected from the crystal structure where the sulfate groups are in a relatively open environment with little or no influence of cations in the direct neighbourhood [12].

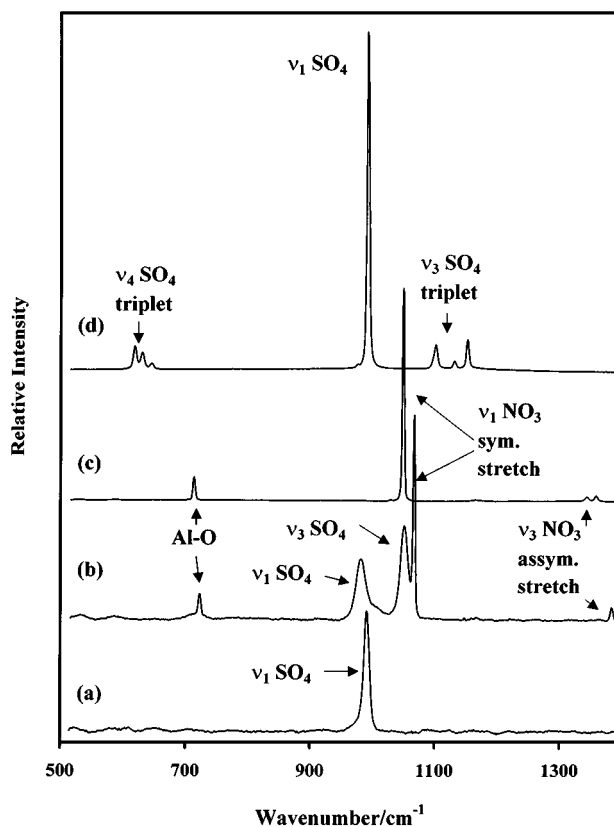


Figure 1 Raman spectra of (a) Al₂(SO₄)₃·xH₂O, (b) Al₁₃ sulfate, (c) Al₁₃ nitrate and (d) Na₂SO₄·xH₂O in the region 500–1400 cm⁻¹.

Kloprogge *et al.* [14, 16] have shown that the basic aluminum sulfate contains a small amount of nitrate still present from the initial hydrolysis of the aluminum solution. Nitrate in crystal structure is known to give strong sharp bands even when present in minor amounts. Therefore the sharp band at 1066 cm⁻¹ as assigned to the ν_1 of the symmetric stretch of nitrate. Compared to the basic aluminum nitrate this band has shifted from 1049 cm⁻¹ in the basic aluminum nitrate to 1066 cm⁻¹ in the basic aluminum sulfate containing traces of nitrate. This indicates that the nitrate is not incorporated in the crystal structure on the sulfate position, but is expected to be present as an impurity. The small band at 1384 cm⁻¹ is assigned to the asymmetric

TABLE I Band component analysis of the basic aluminum sulfate Raman spectrum in the 950–1050 cm⁻¹ region in comparison to hydrated sodium and hydrated aluminum sulfate

| Sample | Band position (cm ⁻¹) | Bandwidth (cm ⁻¹) | Band intensity (%) | Suggested assignment |
|--|-----------------------------------|-------------------------------|--------------------|--------------------------------------|
| Al ₁₃ sulfate | 981 | 17 | 26.5 | ν_1 SO ₄ |
| | 1004 | 40 | 14.1 | Not known |
| | 1051 | 15 | 36.8 | ν_3 SO ₄ |
| | 1066 | 4 | 22.6 | ν_1 NO ₃ sym. stretch |
| Al ₂ (SO ₄) ₃ ·xH ₂ O | 991 | 10 | 100.0 | ν_1 SO ₄ |
| Na ₂ SO ₄ ·xH ₂ O | 992 | 5 | 79.6 | ν_1 SO ₄ |
| | 1101 | 6 | 10.0 | ν_3 SO ₄ triplet |
| | 1131 | 5 | 2.2 | |
| | 1152 | 5 | 8.1 | |

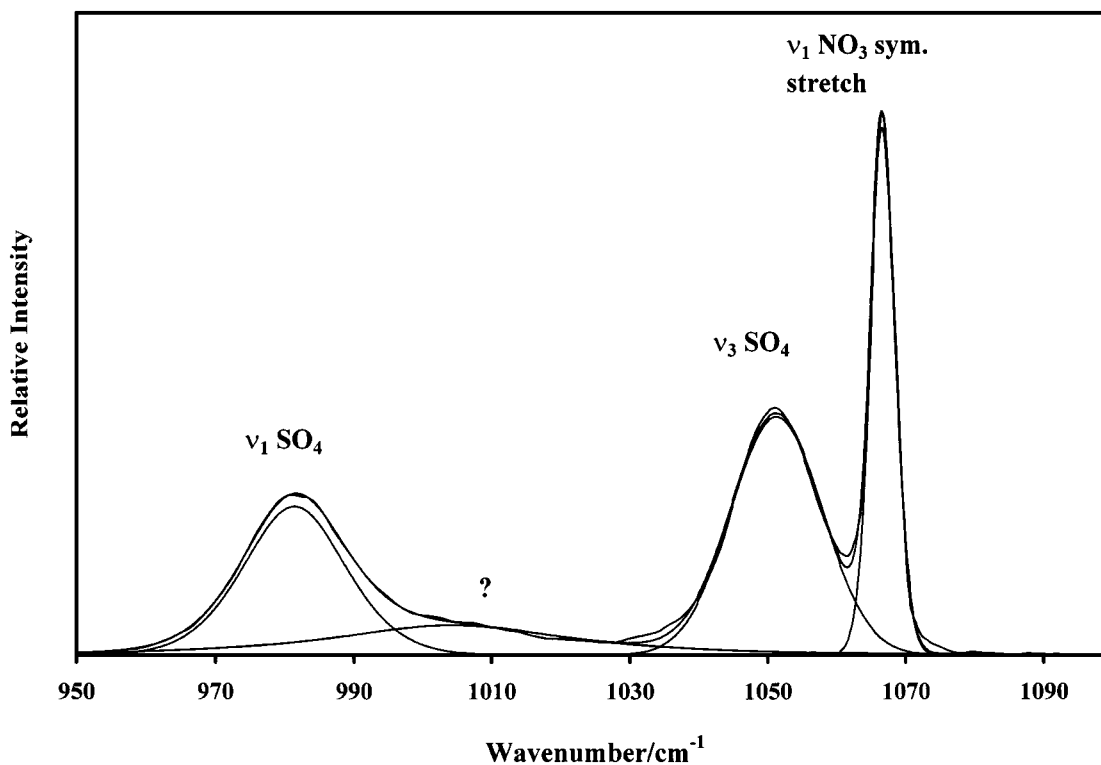


Figure 2 Band component analysis of the basic aluminum sulfate in the 950–1100 cm^{-1} region.

stretching mode of the nitrate comparable to the double band in the Al_{13} nitrate spectrum. At this moment there is no explanation for the occurrence of a double band in the Al_{13} nitrate spectrum, but it may indicate two inequivalent sites in the crystal structure. This assumption requires further detailed research on the crystal structure and the accompanying spectral phenomena.

Band component analysis of this spectrum in the region between 950 and 1100 cm^{-1} (Fig. 2, Table I) reveal a third broad band at 1004 cm^{-1} with a bandwidth of 40 cm^{-1} . The two sulfate bands at 981 and 1051 cm^{-1} have bandwidths of 17 and 16 cm^{-1} respectively. The nitrate band at 1066 cm^{-1} has a bandwidth of 4 cm^{-1} . The band intensities of the two sulfate bands ν_1/ν_3 represent a ratio of 0.72, which is much lower than the ratio ν_1/ν_3 (triplet) of approximately 4 for the hydrated sodium sulfate. The bandwidth of the ν_1 of the sulfate group in the basic aluminum sulfate is approximately 17 cm^{-1} , which is broader than those of the hydrated sodium sulfate (4 cm^{-1}) and hydrated aluminum sulfate (10 cm^{-1}).

At the low frequency region of the Raman spectra of the basic aluminum sulfate and nitrate a low intensity band at 724 and 715 cm^{-1} , respectively for the sulfate and the nitrate, can be observed, which is absent in the spectra of the hydrated sodium sulfate and hydrated aluminum sulfate. Therefore, it is suggested that this band must be associated with the Al_{13} Keggin structure and is assigned as an Al–O mode present in a polymerised form of Al–O–Al bonds as are present in the Al_{13} structure.

4. Conclusions

The Raman spectrum of basic aluminum sulfate is dominated by two broad bands which are assigned to the ν_1

and ν_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} is assigned to an Al–O mode of the polymerised Al_{13} Keggin structure. The sharp band at 1066 and the minor band at 1384 cm^{-1} are 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 ν_1 symmetric stretching and ν_3 asymmetric stretching modes.

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