

# Near-infrared spectroscopic study of [AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>23</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>7+</sup>-O-Si(OH)<sub>3</sub> nitrate crystals formed by forced hydrolysis of Al<sup>3+</sup> in the presence of TEOS

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## Abstract

The polymer [AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>23</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>7+</sup>-O-Si(OH)<sub>3</sub> was prepared by forced hydrolysis of Al<sup>3+</sup> up to an OH/Al molar ratio of 2.0 in the presence of monomeric orthosilicic acid. Crystalline material was obtained by slow evaporation. Although the near-infrared spectra of the Al<sub>13</sub>-sulfate and Al<sub>13</sub>-O-Si(OH)<sub>3</sub> are very similar, there are differences related to the bonding of the -O-Si(OH)<sub>3</sub> group to the Al<sub>13</sub>-unit. The strong complex of bands around 7000 cm<sup>-1</sup> associated with the overtones and combination bands of the OH-stretching modes for Al<sub>13</sub>-sulfate is much weaker for Al<sub>13</sub>-O-Si(OH)<sub>3</sub> and the opposite is true for the complex of bands around 5000 cm<sup>-1</sup> associated with the water overtone and combination modes, suggesting that the outer OH-groups of the Al<sub>13</sub>-unit are involved in the formation of the new Al<sub>13</sub>-O-Si(OH)<sub>3</sub> units. A weak band around 7370–7631 cm<sup>-1</sup> is interpreted as the overtone of the Si–OH stretching vibration around 3740 cm<sup>-1</sup>. A low intensity band, absent for Al<sub>13</sub>-sulfate and -nitrate is observed around 5550–5570 cm<sup>-1</sup> and is interpreted as the overtone of the OH-stretching mode of the OH-groups in the vicinity of the central AlO<sub>4</sub> in the Al<sub>13</sub>-unit around 2890–2935 cm<sup>-1</sup>. The interaction between the -O-Si(OH)<sub>3</sub> group and the Al<sub>13</sub>-unit has a small influence on other bands like the combination modes of water in the 4400–4800 cm<sup>-1</sup> region, which show a small shift towards higher wavenumbers. The internal OH-groups in the Al<sub>13</sub>-complex are relatively shielded by the water molecules and therefore do not reflect the influence of the -O-Si(OH)<sub>3</sub> in their band positions. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Aluminium; Forced hydrolysis; Infrared spectroscopy; Near-infrared spectroscopy; Tetraethyl orthosilicate (TEOS)

## 1. Introduction

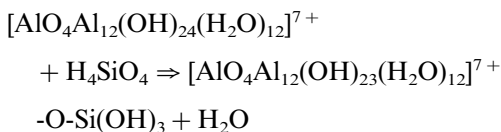
The hydrolysis of Al<sup>3+</sup> is rather complex and many species can be formed including monomers, dimers, various oligomers and large polymers

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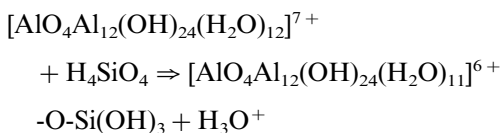
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such as the Keggin structure  $\text{Al}_{13}$  or  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{23}(\text{H}_2\text{O})_{12}]^{7+}$  [1–3]. The existence of this polymer was first proven by X-ray diffraction of the associated sulfate salt by Johansson and co-workers [4–7]. The formation of this polymer has been extensively studied by means of mainly  $^{27}\text{Al}$  NMR (see e.g. references in [1,8]).

Since the oil-crisis in the early 1970s interest arose in using this  $\text{Al}_{13}$  polymer as a pillaring agent in clays, because these pillared clays exhibit physicochemical properties important for catalysts and molecular sieves [9–12]. In order to create larger pore sizes larger pillars have to be incorporated in the clay. One way of achieving this is to react one or more groups like  $\text{Si}(\text{OH})_4$  with the outer OH-groups of the  $\text{Al}_{13}$  [13–20]. These solutions contained hydroxy–Si–Al polymers, which differed from the  $\text{Al}_{13}$  structure. For the reaction of orthosilicic acid with  $\text{AlCl}_3$  and  $\text{NaOH}$  several possible mechanisms have been discussed by Luciuk and Huang [21]. Wada and Wada [22] and Sterte and Shabtai [23] suggested the following mechanism for the reaction of  $\text{Al}_{13}$  with orthosilicic acid:



Wada and Wada [22] observed a slight increase in acidity, which they explained by a small contribution of a secondary reaction:



In an earlier study Klopogge and Frost [24] reported the Raman and infrared (IR) spectra of  $\text{Al}_{13}$ -O-Si(OH)<sub>3</sub> nitrate. The spectra were characterised by the similar bands as the pure  $\text{Al}_{13}$  nitrate. The IR spectrum of the  $\text{Al}_{13}$  crystals without any  $\text{SiO}(\text{OH})_3$  added, indicated that previous assignments of the bands between 450 and 800  $\text{cm}^{-1}$  to the sulfate in the crystal structure of basic aluminium sulfate [25] were not correct for the  $\text{Al}_{13}$  in this study. These bands are more likely to correspond with deformation bands within the

Al octahedra of the  $\text{Al}_{13}$  complex. Upon increasing the Si/Al ratio, a part of the nitrate was replaced as evidenced by the decrease in intensity of one of each set of double nitrate bands in both the Raman and IR spectra. The incorporation of  $\text{SiO}(\text{OH})_3$  in the crystal structure resulted in the formation of new IR bands at 3740  $\text{cm}^{-1}$  assigned to silanol groups, 1106  $\text{cm}^{-1}$  assigned to Si-O stretching mode and a band at 724  $\text{cm}^{-1}$  assigned to Si-O-Al deformation mode. The formation of the  $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{23}(\text{H}_2\text{O})_{12}]^{7+}$ -O-Si(OH)<sub>3</sub> was therefore thought to proceed via the replacement of incorporated nitrate groups in the  $\text{Al}_{13}$  structure instead of via the hydroxyl groups.

The near-infrared (NIR) spectral region has been defined by Kaye [26,27] to extend from 700 to 3500 nm (14 285–2860  $\text{cm}^{-1}$ ). The only fundamental vibrations in the NIR region between 4000 and 10 000  $\text{cm}^{-1}$  are those associated with hydrogen atoms associated with hydroxyl groups or water in the case of minerals and inorganic compounds like aluminium sulfates. Rossman [28] reported average band positions for hydroxyl and water in the NIR region around 4200  $\text{cm}^{-1}$  as being due to Al-OH motions, 5200  $\text{cm}^{-1}$  as the  $\text{H}_2\text{O}$  combination mode (bend + stretch) and around 7100  $\text{cm}^{-1}$  as the first OH stretch overtone. This means that NIR spectroscopy is a very suitable technique to study compounds as the  $\text{Al}_{13}$  and  $\text{Al}_{13}$ -O-Si(OH)<sub>3</sub> salts, which contains both water and OH groups in the  $\text{Al}_{13}$  Keggin structure combined with additional crystal water in the structure, and obtain more information about the local environments involved.

Very recently Klopogge et al. [29] reported the near-infrared spectra of the  $\text{Al}_{13}$ -sulfate and nitrate salts. Although the near-infrared spectra of the  $\text{Al}_{13}$ -sulfate and nitrate were very similar indicating similar crystal structures, there were minor differences related to the strength with which the crystal water molecules are bonded to the salt groups. The interaction between crystal water and nitrate is stronger than with the sulfate as reflected by the shift of the crystal water band positions from 6213, 4874 and 4553  $\text{cm}^{-1}$  for the  $\text{Al}_{13}$ -sulfate towards 5925, 4848 and 4532  $\text{cm}^{-1}$  for the nitrate. A reversed shift from 5079 and 5037  $\text{cm}^{-1}$  for the sulfate towards 5238 and 5040

$\text{cm}^{-1}$  for the nitrate for the water molecules in the  $\text{Al}_{13}$  indicate that the nitrate  $\text{Al}_{13}$  bond is weakened due to the influence of the crystal water on the nitrate. The Al-OH bond in the  $\text{Al}_{13}$  complex is not influenced by changing the salt group due to the shielding by the water molecules of the  $\text{Al}_{13}$  complex.

This paper forms a continuation of our study of the vibrational spectroscopy of  $\text{Al}_{13}$ -salts both with and without  $\text{Si}(\text{OH})_4$ . To date the near-infrared spectrum of  $\text{Al}_{13}\text{-O-Si}(\text{OH})_3$  has not been studied or published. Therefore, the objective of this paper is to report extensively the near-infrared (NIR) spectra obtained at 298 K of  $\text{Al}_{13}\text{-O-Si}(\text{OH})_3$  prepared by forced hydrolysis of  $\text{Al}^{3+}$  in the presence of tetraethyl orthosilicate (TEOS) at various Si/Al molar ratios and to compare them  $\text{Al}_{13}$ -sulfate.

## 2. Experimental

The preparation of the solutions was carried out by a method comparable to the method described by Wada and Wada [22] and Sterte and Shabtai [23]. Monomeric orthosilicic acid solutions were prepared by dilution in deionised water of tetraethyl orthosilicate (TEOS, Merck-Schuchardt no. 800658) dissolved in 50 ml ethanol. The  $\text{Si}(\text{OH})_4$  solutions had concentrations of 0.125, 0.250, 0.375, and 0.500 M. Equal amounts of 0.500 M  $\text{Al}(\text{NO}_3)_3$  solutions (Merck no. 1063) were added to the  $\text{Si}(\text{OH})_4$  solutions and to a solution without  $\text{Si}(\text{OH})_4$ , resulting in solutions having Si/Al mol ratios of 0.00, 0.25, 0.50, 0.75 and 1.00. A 0.500 M NaOH (Merck no. 6498 pellets) solution was then injected with  $1 \text{ ml min}^{-1}$  in the Si/Al solutions under vigorous stirring until an OH/Al mol ratio of 2.0 was reached. The solutions were aged in polyethylene bottles until all the solutions were completely evaporated.

The NIR spectroscopy analyses were performed on a Perkin-Elmer System 2000 NIR-FT Raman spectrometer equipped with a Spectron Laser Systems SL301 N&YAG laser operating a wavelength of 1064 nm. For the samples 32 scans were accumulated at a spectral resolution of  $16 \text{ cm}^{-1}$  using a mirror velocity of  $0.2 \text{ cm}^{-1} \text{ s}^{-1}$  to get an acceptable signal/noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, 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 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

Table 1 shows the band component analysis of the infrared spectra of the silica modified  $\text{Al}_{13}$  in comparison to the pure  $\text{Al}_{13}$ -nitrate and -sulfate. The preparation of  $\text{Al}_{13}$  by forced hydrolysis of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  by NaOH in the presence of monomeric orthosilicic acid results in some significant changes in both the Raman and FT-IR spectra of this complex material [24]. Changes in the Raman spectra reveal upon increasing Si/Al ratio the replacement of some of the nitrate groups as evidenced by the decrease in intensity of one of each of set of double nitrate bands, especially easily observable at  $1358 \text{ cm}^{-1}$ . This is in agreement with the FT-IR observations where the most important changes are observed in the nitrate double bands  $\nu_{2a}$ , and  $\nu_{2b}$  at  $826$  and  $830 \text{ cm}^{-1}$ ,  $\nu_1$  at  $1046 \text{ cm}^{-1}$  and  $\nu_3$  around  $1383 \text{ cm}^{-1}$ . The  $\nu_2$  bands show behaviour similar to that described for the nitrate bands in the Raman spectra with a strong decrease of the  $\nu_{2a}$  while the  $\nu_{2b}$  remains more or less constant. The incorporation of a unit like  $\text{SiO}(\text{OH})_3$  is indicated by the observation of a silanol band around  $3740 \text{ cm}^{-1}$  and a corresponding Si-O stretching band at  $1106 \text{ cm}^{-1}$ . More indirect minor changes in the broad complex around  $450\text{--}800 \text{ cm}^{-1}$  indicate the possible formation of new Al-O-Si bonds evidenced by a band around  $724 \text{ cm}^{-1}$  when the monomeric orthosilicic acid is added to the solution.

Band component analysis of the OH-stretching region reveals bands around roughly 2890–2935, 3163–3245 and 3449–3465  $\text{cm}^{-1}$  depending on the Si/Al ratio, attributed to OH groups in the vicinity of the central  $\text{AlO}_4$  group, OH of  $\text{H}_2\text{O}$  and OH of the outer octahedral OH groups, respectively. The addition of monomeric orthosilicic acid results in the formation of a very small new band around 3740  $\text{cm}^{-1}$  ascribed to newly formed silanol groups in the complex  $\text{Al}_{13}$  crystals [24]. Associated with these stretching modes there are two water bending modes observed around 1633 and 1676  $\text{cm}^{-1}$  and Al-OH bending modes around 1164, 1076, 984 and 967  $\text{cm}^{-1}$  for the silica modified  $\text{Al}_{13}$ .

Near-infrared (NIR) spectroscopy is also known as ‘proton’ infrared spectroscopy as it covers the spectral region in which all the overtone and combination bands of vibrations involving hydrogen appear. In the case of  $\text{Al}_{13}$ -salts this means the overtone and combination bands of the

OH-groups and  $\text{H}_2\text{O}$  from the 12 octahedra plus crystal water outside the  $\text{Al}_{13}$  units. Roughly three spectral regions can be recognised: (a) the high frequency region around 7000  $\text{cm}^{-1}$ , (b) the region between 4800 and 5400  $\text{cm}^{-1}$  and (c) the region between 4000 and 4800  $\text{cm}^{-1}$ . Fig. 1 shows the NIR spectra of the  $\text{Al}_{13}$  salts formed in the presence of increasing amounts of orthosilicic acid. Table 2 summarises the band component analysis of the spectra shown in Figs. 1 and 2.

A first general observation is that the strong complex of bands around 7000  $\text{cm}^{-1}$  associated mainly with the overtones and combination bands of the OH-stretching modes for the  $\text{Al}_{13}$ -sulfate is much weaker for the  $\text{Al}_{13}$ -O-Si(OH)<sub>3</sub> crystals and the opposite is true for the complex of bands around 5000  $\text{cm}^{-1}$  associated with the water overtone and combination modes. This suggests that the OH-groups of the  $\text{Al}_{13}$  unit are more involved in the formation of the new  $\text{Al}_{13}$ -O-Si(OH)<sub>3</sub> units than expected based on our earlier

Table 1

Band component analysis of the infrared spectra of  $\text{Al}_{13}$ -salts with and without silica [24]

$\text{Al}_{13}$ -O-Si(OH) <sub>3</sub> ( $\text{cm}^{-1}$ )	$\text{Al}_{13}$ sulfate ( $\text{cm}^{-1}$ )	$\text{Al}_{13}$ nitrate ( $\text{cm}^{-1}$ )	Assignment
3740			Si-OH OH-stretch
3449–3465	3434	3433	OH-stretch (1)
3163–3245	3068	3192	$\text{H}_2\text{O}$ OH-stretch (2)
2890–2935			OH-stretch Al-OH vicinity $\text{AlO}_4$
1763		1764	$\text{NO}_3$ combination band ( $\nu_1 + \nu_4$ )
1676	1688	1670	$\text{H}_2\text{O}$ bend (1)
1633	1639	1629	$\text{H}_2\text{O}$ bend (2)
1383	1384	1387	$\nu_3 \text{NO}_3$
1164		1163	Al-OH <sub>2</sub> bend (1)
1114	1113		$\nu_3 \text{SO}_4$
1106			Si-O stretching SiO(OH) <sub>3</sub>
1076	1089		$\nu_3 \text{SO}_4/\text{Al-OH}_2$ bend (2)
1047		1050	$\nu_1 \text{NO}_3$
984	990		$\nu_1 \text{SO}_4/\text{Al-OH}_2$ bend (3)
967		981	Al-OH <sub>2</sub> bend (4)
	895		Unknown
826/830 double	838	823	$\nu_2 \text{NO}_3$
767–779		776	$\nu_4 \text{NO}_3$
726–750			Al-O-Si
683–706	723	702	Al-O antisymmetric stretch
639–648		620	Al-O symmetric stretch
593–606	620		$\nu_4 \text{SO}_4$
549–552	552		$\nu_4 \text{SO}_4$
		561	Unknown
F-494–522	491		Unknown

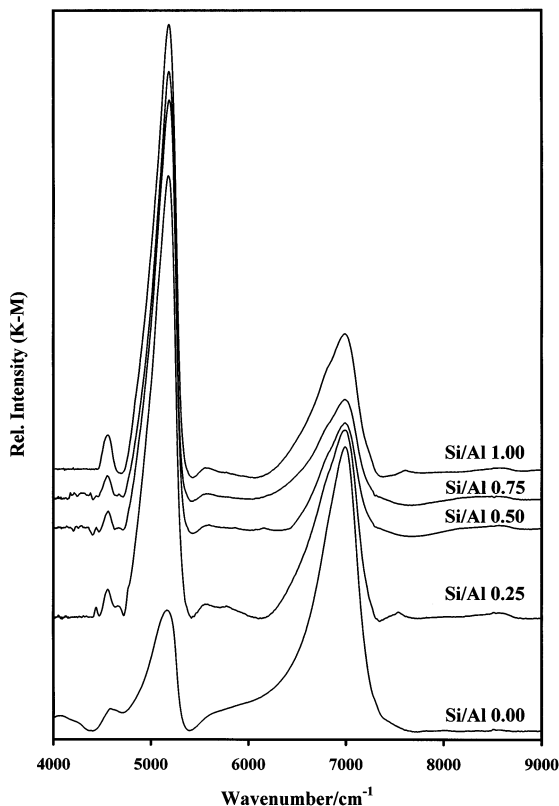


Fig. 1. Near-infrared spectra of  $\text{Al}_{13}\text{-O-Si(OH)}_3$  formed by forced hydrolysis of  $\text{Al}^{3+}$  in the presence of increasing amounts of orthosilicic acid from Si/Al molar ratio 0.00 to 1.00.

observations in the infrared and Raman spectra [24], where it was assumed that the attachment of the  $\text{Si(OH)}_4$  units proceeded via the replacement of incorporated nitrate groups in the  $\text{Al}_{13}$  structure. In addition to the three bands associated with the OH-stretching modes of the Al-OH and  $\text{H}_2\text{O}$  there is a fourth weak band around  $7370\text{--}7631\text{ cm}^{-1}$  not seen for the normal  $\text{Al}_{13}$ -salts, which is interpreted as the first overtone of the Si-OH stretching vibration around  $3740\text{ cm}^{-1}$ .

Another low intensity band, absent for the  $\text{Al}_{13}$ -sulfate and -nitrate, is observed around  $5550\text{--}5570\text{ cm}^{-1}$  and is interpreted as the overtone of the OH-stretching mode of the OH-groups in the vicinity of the central  $\text{AlO}_4$ -tetrahedron in the  $\text{Al}_{13}$  unit around  $2890\text{--}2935\text{ cm}^{-1}$ . However, this band is very close to and overlapping with an-

other weak band around  $5700\text{--}5800\text{ cm}^{-1}$ , which previously has been attributed to the overtone of the AlOH bending modes 3 or 4. The absence of the  $2900\text{ cm}^{-1}$  band however suggests that the above interpretation is correct. This observation also supports the presence of the weaker bands around  $7000\text{ cm}^{-1}$  being caused by the reaction of the monomeric orthosilicic acid with the outer OH-groups of the  $\text{Al}_{13}$ -unit instead of with the incorporated nitrate groups. Removal of the outer OH-groups due to the replacement with the  $-\text{O-Si(OH)}_3$  group seems to increase the visibility of other weak bands like the overtone of the Al-OH bending mode 3 or 4.

A significant difference is visible between the  $\text{Al}_{13}$ -sulfate and the  $\text{Al}_{13}\text{-O-Si(OH)}_3$  NIR spectra in the low frequency region between  $4400$  and  $4800\text{ cm}^{-1}$ . The  $\text{Al}_{13}$ -sulfate shows a broad band which, based on band component analysis, contains actually two bands around  $4553$  and  $4641\text{ cm}^{-1}$  attributed to the combination modes of  $\text{H}_2\text{O}$  (bend 2 + stretch 2) crystal  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  (bend 1 + stretch 2)  $\text{Al}_{13}$  + crystal  $\text{H}_2\text{O}$  [29]. The  $\text{Al}_{13}\text{-O-Si(OH)}_3$  spectrum reveals three clearly developed bands around  $4441\text{--}4444$ ,  $4555\text{--}4562$  and  $4660\text{--}4673\text{ cm}^{-1}$ . The latter two are thought to be identical to the two observed for the  $\text{Al}_{13}$ -sulfate although slightly shifted towards higher wavenumbers due to the presence of the  $-\text{O-Si(OH)}_3$  groups in the vicinity. However, the band at  $4441\text{--}4444\text{ cm}^{-1}$  was not observed before and is thought to represent a combination mode of the AlOH (stretch 1 + bend 3 or 4). As already indicated above the replacement of the outer OH-groups in the  $\text{Al}_{13}$ -unit increases the visibility of these types of weak bands in the near-infrared region.

#### 4. Conclusions

Near-infrared spectroscopy forms a strong tool in addition to the conventional infrared and Raman spectroscopy to get a better understanding of the structure of  $\text{Al}_{13}$ -salts including modified  $\text{Al}_{13}$ -complexes such as  $\text{Al}_{13}\text{-O-Si(OH)}_3$  and especially of the hydroxyl groups and various water molecules in the  $\text{Al}_{13}$  Keggin structure and in the

Table 2

Band component analysis of the NIR spectra of  $\text{Al}_{13}$  sulfate and  $\text{Al}_{13}$  prepared in the presence of orthosilicic acid in the region 4300–8000  $\text{cm}^{-1}$

$\text{Al}_{13}$ sulfate ( $\text{cm}^{-1}$ [29])	Si/Al 0.25 ( $\text{cm}^{-1}$ )	Si/Al 0.50 ( $\text{cm}^{-1}$ )	Si/Al 0.75 ( $\text{cm}^{-1}$ )	Si/Al 1.00 ( $\text{cm}^{-1}$ )	Assignment
7018	7538	7370	7395	7631	Overtone OH-stretch Si-OH
6777	7033	7024	7027	7022	Overtone OH-stretch (1) AlOH
6213	6833	6823	6835	6816	Combination OH-stretch (1 + 2) AlOH + crystal $\text{H}_2\text{O}$
5703	6537	6560	6557	6549	Overtone OH-stretch (2) crystal $\text{H}_2\text{O}$
5236	5758	5788	5749	5727	Overtone AlOH(3/4) bend
5158	5558	5575	5579	5571	Overtone OH-stretch AlOH vicinity $\text{AlO}_4$
5047	5211	5223	5223	5224	$\text{H}_2\text{O}$ combination (bend 1 + stretch 1) $\text{Al}_{13}$
4874	5139	5168	5178	5172	$\text{H}_2\text{O}$ combination (bend 2 + stretch 1) crystal $\text{H}_2\text{O}$ + $\text{Al}_{13}$
4641	4981	5055	5086	5037	Overtone $\text{H}_2\text{O}$ bend (1) $\text{Al}_{13}$
4553	4837	4877	4912	4864	Overtone $\text{H}_2\text{O}$ bend (2) crystal $\text{H}_2\text{O}$
	4660	4667	4673	–	Combination $\text{H}_2\text{O}$ (bend 1 + stretch 2) $\text{Al}_{13}$ + crystal $\text{H}_2\text{O}$
	4561	4562	4555	4556	Combination $\text{H}_2\text{O}$ (bend 2 + stretch 2) crystal $\text{H}_2\text{O}$
	4441	4443	4444	–	Combination AlOH (stretch 1 + bend 3 or 4)

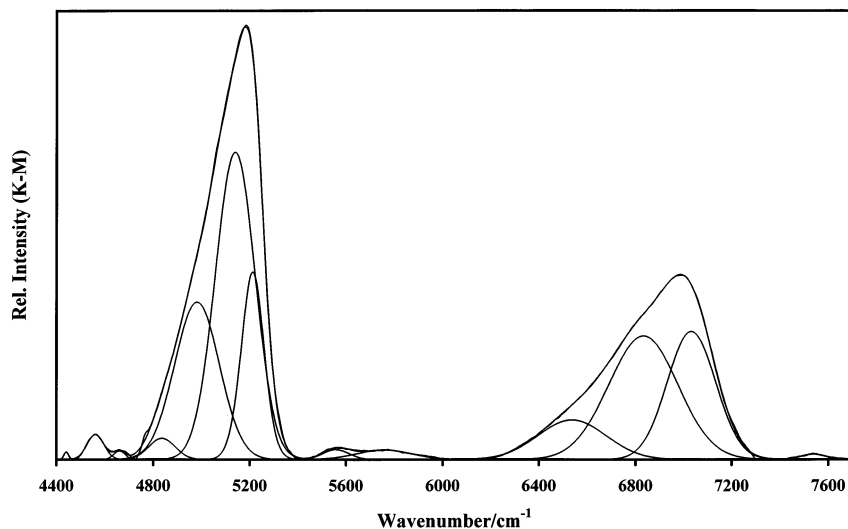


Fig. 2. Band component analysis of the near infrared spectrum in the 4400–7700  $\text{cm}^{-1}$  region of  $\text{Al}_{13}$ -O-Si(OH)<sub>3</sub> formed at a Si/Al molar ratio of 0.25.

structure outside the  $Al_{13}$  complex. Although the near-infrared spectra of the  $Al_{13}$ -sulfate and  $Al_{13}$ -O-Si(OH)<sub>3</sub> are very similar, there are differences related to the bonding of the -O-Si(OH)<sub>3</sub> group to the  $Al_{13}$ -unit thereby replacing a part of the outer OH-groups instead of nitrate groups as reported in earlier work. The interaction between -O-Si(OH)<sub>3</sub> group and the  $Al_{13}$ -unit has a small but measurable influence on other overtone and combination bands. This is reflected in a small shift towards higher wavenumbers of the bands associated with the combination modes of water in the 4400–4800  $cm^{-1}$  region. The internal hydroxyl groups in the  $Al_{13}$  complex are relatively shielded by the water molecules and therefore do not reflect the influence of the -O-Si(OH)<sub>3</sub> in their band positions.

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