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## Raman spectroscopy of the sampleite group of minerals

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### Abstract:

Raman and infrared spectroscopy has enabled insights into the molecular structure of the sampleite group of minerals. These minerals are based upon the incorporation of either phosphate or arsenate with chloride anion into the structure and as a consequence the spectra reflect the bands attributable to these anions, namely phosphate or arsenate with chloride. The sampleite vibrational spectrum reflects the spectrum of the phosphate anion and consists of  $\nu_1$  at 964,  $\nu_2$  at 451  $\text{cm}^{-1}$ ,  $\nu_3$  at 1016 and 1088 and  $\nu_4$  at 643, 604, 591 and 557  $\text{cm}^{-1}$ . The lavendulan spectrum consists of  $\nu_1$  at 854,  $\nu_2$  at 345  $\text{cm}^{-1}$ ,  $\nu_3$  at 878  $\text{cm}^{-1}$  and  $\nu_4$  at 545  $\text{cm}^{-1}$ . The Raman spectrum of lemanskiite is different from that of lavendulan consistent with a different structure. Low wavenumber bands at 227 and 210  $\text{cm}^{-1}$  may be assigned to CuCl TO/LO optic vibrations. Raman spectroscopy identified the substitution of arsenate by phosphate in zdenekite and lavendulan.

**Key Words-** sampleite, lavendulan, zdenekite, lemanskiite, Raman spectroscopy

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### INTRODUCTION

Phosphates and arsenate minerals of copper are very common. Among these minerals are those of the sampleite group<sup>1-5</sup> including sampleite ( $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ ), lavendulan ( $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ ), zdenekite ( $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ ), and the polymorph of lavendulan known as lemanskiite.<sup>6-8</sup> The minerals are often found in arid climates, and in caves derived from copper sulphides in cave walls and the phosphate from bat guano. Some are known as post mining species.<sup>7,9</sup> Also, some have been found as alteration products in ancient slag heaps.<sup>10,11</sup> Further it is certain that some of these minerals are of archaeological significance<sup>12</sup> and it is apparent that they were used for colourant effects in cosmetics of the ancient Egyptians.<sup>13</sup> Certainly the appearance of the minerals provides various shades of blue and blue-green.

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Raman spectra of the tetrahedral phosphate and arsenate anions in aqueous systems are well known<sup>14-19</sup>. Raman spectra of aqueous phosphate oxyanions show the symmetric stretching mode ( $\nu_1$ ) at  $938\text{ cm}^{-1}$ , the antisymmetric stretching mode ( $\nu_3$ ) at  $1017\text{ cm}^{-1}$ , the symmetric bending mode ( $\nu_2$ ) at  $420\text{ cm}^{-1}$  and the  $\nu_4$  mode at  $567\text{ cm}^{-1}$ . The infrared spectra of minerals containing the arsenate anion have been published. Farmer reported the vibrational spectra of the phosphate minerals: libethenite, cornetite and pseudomalachite<sup>20</sup>. The pseudomalachite  $[\text{Cu}^{2+}_5(\text{PO}_4)_2(\text{OH})_4]$  vibrational spectrum consists of  $\nu_1$  at  $953$ ,  $\nu_2$  at  $422$  and  $450\text{ cm}^{-1}$ ,  $\nu_3$  at  $1025$  and  $1096$  and  $\nu_4$  at  $482$ ,  $530$ ,  $555$  and  $615\text{ cm}^{-1}$ . Libethenite  $[\text{Cu}^{2+}_2(\text{PO}_4)(\text{OH})]$  vibrational modes occur at  $960$  ( $\nu_1$ ),  $445$  ( $\nu_2$ ),  $1050$  ( $\nu_3$ ) and  $480$ ,  $522$ ,  $555$ ,  $618$  and  $637\text{ cm}^{-1}$  ( $\nu_4$ ). Cornetite  $[\text{Cu}^{2+}_3(\text{PO}_4)_2(\text{OH})_3]$  vibrational modes occur at  $960$  ( $\nu_1$ ),  $415$  and  $464$  ( $\nu_2$ ),  $1000$ ,  $1015$  and  $1070$  ( $\nu_3$ ) and  $510$ ,  $527$ ,  $558$ ,  $582$ ,  $623$  and  $647\text{ cm}^{-1}$  ( $\nu_4$ )<sup>21</sup>. The symmetric stretching vibration of the arsenate anion ( $\nu_1$ ) is observed at  $810\text{ cm}^{-1}$  coincident with the position of the asymmetric stretching mode ( $\nu_3$ ). The symmetric bending mode ( $\nu_2$ ) is observed at  $342\text{ cm}^{-1}$  and the out-of-plane bending modes ( $\nu_4$ ) is observed at  $398\text{ cm}^{-1}$ . Of all the tetrahedral oxyanion spectra, the wavenumbers of the arsenate vibrations are lower than those of any of the other naturally occurring mineral oxyanions. Farmer lists a number of infrared spectra of arsenates including those of annabergite  $[\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ , erythrite  $[\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ , sympleksite  $[\text{Fe}^{2+}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ , and köttigite  $[\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ <sup>20</sup>. The effect on the arsenate ion in a crystal will be to remove the degeneracies and allow splitting of the bands according to factor group analysis. The  $\nu_1$  and  $\nu_3$  bands of annabergite were observed at  $832$  and  $795\text{ cm}^{-1}$ . Bending modes were found at  $510$ ,  $460$  and  $427\text{ cm}^{-1}$  for annabergite. No  $\nu_2$  bands were reported. This is no doubt related to the fact that these bands lie below  $400\text{ cm}^{-1}$ , which makes the measurement by infrared spectroscopy difficult. Two OH stretching vibrations were observed at  $3430$  and  $3160\text{ cm}^{-1}$  for annabergite. Several unassigned bands were listed.

Sampleite and its arsenate analogue, lavendulan, are isomorphous, monoclinic, pseudo-orthorhombic and pseudo-tetragonal. The point group is  $2/m$ . The other minerals in the group namely zdenekite and lemanskiite are claimed to be tetragonal but the space group and structures have been published.<sup>22,23</sup> Table 1 shows the status of our knowledge of the crystallography of the sampleite mineral group.

Whilst infrared spectra of a number of copper arsenate and phosphate minerals have been reported, few studies of the sampleite group have been undertaken. It remains to be proven whether Raman spectroscopy can help in the elucidation of the sampleite structures. In this work we report the Raman spectra of several members of the sampleite group at  $298$  and  $77\text{ K}$  and comment on the data in light of structural characterisations.

## **EXPERIMENTAL**

### ***The minerals***

Minerals used in this research were supplied by The Museum of South Australia. Lavendulan registered number G20750 originated from the Dome Rock Copper Mine, South Australia.

Lavendulan (M30899) originated from the Alice Mary Mine, Kundip, Western Australia.

Lemanskiite registered number G26439 originated from the El Guanqco Mine, Antofagsta, Chile.

Sampleite (G26485) came from the E26 North Parks Gold Mine, Parks, NSW, Australia.

Sampleite was also sourced from lake Boga, Victoria, Australia.

Zdenekite (G26393) was sourced from Block 14 Opencut, Broken Hill, NSW, Australia.

Zdenekite was also obtained from Pequa rare minerals and was sourced from Cap garonne Mine near le Pradet (12 km west of Toulon) France<sup>6</sup>.

Minerals were analysed for constituent elements by SEM/EDX and crystal morphology was examined by SEM methods.

### ***Infrared spectroscopy***

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000 to 525 cm<sup>-1</sup> range were obtained by the co-addition of 64 scans with a resolution of 4 cm<sup>-1</sup> and a mirror velocity of 0.6329 cm/s.

### ***Raman microprobe spectroscopy***

Crystals were orientated on a polished metal surface on the stage of an Olympus BHSM microscope equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Details of the spectroscopy have been published<sup>24-28</sup>.

Spectroscopic 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 Gauss-Lorentz 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.

## **RESULTS AND DISCUSSION**

### **Electron Microscopy**

SEM pictures of sampleite, lavendulan, lemanskiite and zdenekite are shown in Figure 1. The sampleite SAMPLE (Figure 1a) consists of thin crystals flattened on {010} and elongated along {001}. In contrast, crystals of lavendulan consists of rosettes of plates FORMING botryoidal crusts (Figure 1b). The morphology of

lemanskiite resembles that of sampleite (Figure 1c). Electron microscopy shows zdenekite to CONSIST of tabular crystals to 0.1 mm, flattened on {001}, showing forms {001}, {100} and {110}, in spherical aggregates and crusts.

The morphology of lemanskiite more closely resembles that of sampleite (Figure 1c). Electron microscopy shows the zdenekite to be of tabular crystals to 0.1 mm, flattened on the {001} axis showing {001}, {100} and {110} in spherical aggregates and crusts. No substitution of arsenate by phosphate is observed in the sampleite sample. Similarly, the lavendulan sample shows no phosphate substitution. The Lemanskiite similarly shows no substitution by phosphate. Similarly the lavendulan analyses as  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  with no phosphate substitution observed. Some erythrite is observed in the matrix. The lemanskiite is a pure mineral with no substitution by phosphate. The zdenekite analyses as  $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  with some minor substitution of Pb by Ca and by Fe. Thus the minerals lend themselves to analysis by vibrational spectroscopic techniques.

### **Infrared spectroscopy**

The infrared spectra of the hydroxyl stretching region of the four minerals sampleite, lavendulan, lemanskiite and zdenekite are shown in Figure 2. Single crystal X-ray crystallography of sampleite, lavendulan and zdenekite shows that the five water molecules in the crystal are non-equivalent. From an infrared spectroscopic point of view this means that a large number of bands could be expected. This is observed in the spectra of Figure 2 and the data of Table 2. The infrared spectrum of each mineral shows a broad profile made up of a complex set of overlapping bands. The band components are identified in Figure 2. The sampleite IR spectrum shows five overlapping bands at 3567, 3519, 3314, 3166 and 2908  $\text{cm}^{-1}$ , all of which are attributed to water hydroxyl stretching vibrations. It is highly likely that these bands are composed of a significant number of overlapping bands which are not observed through accidental degeneracy. In the infrared spectrum of lavendulan, water hydroxyl stretching vibrations are observed at 3563, 3529, 3433, 3346, 3296, 3220 and 3040  $\text{cm}^{-1}$ . In total seven bands are observed. For lemanskiite bands are observed at 3559, 3515, 3445, 3315, 3194 and 2988  $\text{cm}^{-1}$ . For zdenekite bands are observed at 3443, 3360, 3108 and 2927  $\text{cm}^{-1}$ .

Studies have shown a strong correlation between OH stretching frequencies and both O··O bond distances and H··O hydrogen bond distances<sup>29-32</sup>. Libowitzky (1999) showed that a regression function can be employed relating the above correlations with regression coefficients better than 0.96<sup>33</sup>. The function is  $\nu_1 = 3592 - 304 \times 10^9 \exp(-d(\text{O}-\text{O})/0.1321) \text{ cm}^{-1}$ . What this means in this case is that the variation in the water hydroxyl stretching frequency is a measure of the hydrogen bond strength between the OH unit of the water and the phosphate or arsenate anion. Bands with high wavenumber positions (for example the bands at 3567, 3563 and 3559  $\text{cm}^{-1}$ ) are very weakly hydrogen bonded and the OH distances from the arsenate or phosphate anion are relatively long. Those hydroxyl stretching frequencies which are  $\sim 3000 \text{ cm}^{-1}$  are strongly hydrogen bonded and are associated with shorter hydrogen bonds. Such variation in hydrogen bond strength with OH-AsO<sub>4</sub> distance is also reflected in water HOH bending modes observed at around 1630  $\text{cm}^{-1}$  (Figure 3). The infrared spectrum of sampleite in this region shows two principle bands at 1645

and  $1616\text{ cm}^{-1}$  with a minor band at  $1680\text{ cm}^{-1}$ . The last band is associated with strongly hydrogen bonded water, the band at  $1654\text{ cm}^{-1}$  with relatively strong hydrogen bonded water and the band at  $1616\text{ cm}^{-1}$  with weakly hydrogen bonded water. The infrared spectrum of lavendulan shows four bands in the HOH bending region at  $1648$ ,  $1635$ ,  $1616$  and  $1584\text{ cm}^{-1}$ . The four bands represent variation in hydrogen bonded strength of water in the lavendulan unit cell. The infrared spectrum of zdenekite shows a single band centred upon  $1637\text{ cm}^{-1}$ .

In the infrared spectrum of sampleite a strong broad band is observed at  $957\text{ cm}^{-1}$  and is assigned to the ( $\nu_1$ )  $\text{PO}_4$  symmetric stretching mode (Figure 4). A series of bands is observed at  $995$ ,  $1037$ ,  $1066$ ,  $1102$ ,  $1148$  and  $1171\text{ cm}^{-1}$ , attributed to the  $\nu_3$  antisymmetric  $\text{PO}_4$  stretching modes. The observation of a large number of  $\nu_3$  vibrations is simply a reflection of the symmetry reduction of the  $\text{PO}_4$  unit. The infrared technique used in this work is based upon the use of an ATR diamond cell and bands below  $550\text{ cm}^{-1}$  are not observed, but a band at  $620\text{ cm}^{-1}$  is assigned to the  $\nu_4$  mode. The band at  $789\text{ cm}^{-1}$  is attributed to a water librational mode.

The infrared spectrum of lavendulan shows a broad profile in the  $600$  to  $900\text{ cm}^{-1}$  region (Figure 4). Two overlapping bands are identified at  $764$  and  $784\text{ cm}^{-1}$ ; the former is assigned to the water librational mode equivalent to the  $789\text{ cm}^{-1}$  band of sampleite and the  $784\text{ cm}^{-1}$  band is attributed to the  $\nu_1$  symmetric  $\text{AsO}_4$  stretching mode. Other bands are observed at  $814$ ,  $836$ ,  $861$  and  $884\text{ cm}^{-1}$ . These are attributed to the  $\text{AsO}_4$  antisymmetric stretching vibrations. Low intensity bands are observed at  $1112$  and  $1207\text{ cm}^{-1}$ . The infrared spectrum of lemanskiite displays a reasonably close resemblance to that of lavendulan. Two bands are resolved at  $789$  and  $722\text{ cm}^{-1}$  and are attributed to the  $\text{AsO}_4$  symmetric stretching mode and the water librational mode. A series of bands is observed at  $834$ ,  $862$ ,  $886$ ,  $921$  and  $981\text{ cm}^{-1}$  and may be assigned to  $\text{AsO}_4$  antisymmetric stretching modes. Additional bands are observed at  $1061$  and  $1118\text{ cm}^{-1}$ .

### **Raman spectroscopy**

Raman spectra of the series of sampleite minerals are shown in Figures 5 and 6. The results of the spectroscopic analyses are reported in Table 3. Spectra (a) and (b) are the spectra of sampleite and its polymorph from New South Wales and Victoria, respectively. The spectrum of the sampleite polymorph from Victoria shows intense bands at  $997$  and  $964\text{ cm}^{-1}$  with bands of much less intensity at  $1264$ ,  $1160$  and  $1087\text{ cm}^{-1}$ . The spectrum of the sampleite displays intense bands at  $997$ ,  $962$  and  $924\text{ cm}^{-1}$ . Bands of lesser intensity are observed at  $1269$ ,  $1152$ ,  $1088$  and  $1016\text{ cm}^{-1}$ . The  $924\text{ cm}^{-1}$  band is not observed in the spectrum of the polymorph. The spectra are consistent with known structural differences. The bands listed above are attributed to vibrations of the phosphate anion. One possibility is that the bands in the  $924$  to  $997\text{ cm}^{-1}$  region are due to the  $\nu_1$  symmetric stretching vibration and the bands in the  $1016$  to  $1269\text{ cm}^{-1}$  region are due to the  $\nu_3$  antisymmetric stretching vibrations. In these minerals isomorphous substitution of phosphate and arsenate may readily occur and it is possible that arsenate substitution for phosphate may occur. However no arsenate symmetric stretching bands are observed.

Lemanskiite and lavendulan are closely related species. When X-ray diffraction is undertaken under vacuum identical XRD patterns are obtained (that of

lavendulan). However, the Raman spectra of lemanskiite and lavendulan are different (Figure 5 compare spectra c with d or e). A similar observation may be made in the low wavenumber region. Whilst the spectra of the two are similar, there are undoubted differences; this may be due to the extent of hydration, but this is not certain and it may be that lemanskiite is metastable with respect to and easily transformed to lavendulan.

The Raman spectra of lemanskiite, lavendulan (WA) and lavendulan (SA) display intense bands at 853, 856 and 854  $\text{cm}^{-1}$ , attributed to the  $\text{AsO}_4$  symmetric stretching vibration (Figure 5). The Raman spectrum of zdenekite shows two bands at 879 and 855  $\text{cm}^{-1}$  assigned to  $\text{AsO}_4$  symmetric stretching vibration. Distinct shoulders are observed on the high wavenumber side for lemanskiite and lavendulan (WA) at 878  $\text{cm}^{-1}$ . A probable assignment of this band is the  $\text{AsO}_4$  anti-symmetric stretching vibration. Other low intensity bands are observed at 910  $\text{cm}^{-1}$  for lemanskiite, 981 and 1053  $\text{cm}^{-1}$  for both lavendulan samples. The latter two bands may be attributed to the  $\text{PO}_4$  symmetric stretching vibration. The bands are in a similar position to those of sampleite and some substitution in the sample is thus evident. No bands were identified in the lemanskiite Raman spectrum in this position. Raman spectroscopy has identified some phosphate isomorphic substitution in the lavendulans. No bands were identified in the lemanskiite Raman spectrum in this position. Thus no isomorphic substitution was identified for lemanskiite. A comparison of the Raman spectrum of lavendulan at 298 and 77 K is shown in Figure 7. The Raman spectrum of zdenekite shows an intense band at 1012  $\text{cm}^{-1}$ . This appears to correspond to that of the symmetric stretching band of phosphate in sampleites and therefore is attributed to the isomorphous substitution of arsenate by phosphate in the zdenekite structure. By obtaining the spectrum at 77 K better band separation is obtained and the band at 894  $\text{cm}^{-1}$  is clearly resolved from that at 861  $\text{cm}^{-1}$ . Bandwidths of the 894 and 861  $\text{cm}^{-1}$  bands are 19.4 and 18.2  $\text{cm}^{-1}$ .

The Raman spectra of sampleite and its polymorph in the 200 to 700  $\text{cm}^{-1}$  region are almost identical. An intense band is observed at 643  $\text{cm}^{-1}$  for the polymorph from Victoria and 639  $\text{cm}^{-1}$  for sampleite. This band is assigned to the  $\nu_4$  phosphate bending mode. The bands are broad with halfwidths of 23.0 and 25.6  $\text{cm}^{-1}$ . The width of the bands gives an indication of the variation in out-of-plane bending of the phosphate anion. Although high in wavenumbers, bands in similar positions have been observed for the phosphate in minerals such as cornetite<sup>25,34</sup>. Bands are also observed in this region at 604, 591 and 557  $\text{cm}^{-1}$  for the polymorph from Victoria and at 588 and 548  $\text{cm}^{-1}$  for sampleite from NSW. These bands are also attributed to the  $\nu_4$  bending modes. The most intense band in the low wavenumber region is observed at 451  $\text{cm}^{-1}$  for the polymorph and 455  $\text{cm}^{-1}$  for sampleite. These bands are attributed to the  $\nu_2$   $\text{PO}_4$  in-plane bending mode. Only a single band is observed in the  $\nu_2$  region.

Both the lemanskiite and lavendulan samples show an intense band centred around 545  $\text{cm}^{-1}$ . This band is assigned to the  $\nu_4$   $\text{AsO}_4$  bending vibration. A similar band is observed at 546  $\text{cm}^{-1}$  for zdenekite. The Raman spectrum of zdenekite more closely resembles that of lemanskiite rather than lavendulan. The  $\nu_4$  band is relatively broad with bandwidths of 26.0, 25.5 and 34.9  $\text{cm}^{-1}$  for the lemanskiite, lavendulan (Vic) and lavendulan (NSW). The Raman spectrum of lemanskiite shows an additional band at 479  $\text{cm}^{-1}$ . Both the lavendulan samples show an additional band at

614  $\text{cm}^{-1}$ . One possibility is that this band is due to the librational mode of water. If this is so, then the absence of this peak is noted for lemanskiite. The Raman spectrum of lemanskiite shows an intense band at 345  $\text{cm}^{-1}$ . This band is attributed to the  $\nu_2$   $\text{AsO}_4$  bending mode. The band is observed at 332  $\text{cm}^{-1}$  for zdenekite. The position is very close to that of the aqueous arsenate anion. For the two lavendulans, bands are observed at around 406 and 342  $\text{cm}^{-1}$  and are assigned to the  $\nu_2$   $\text{AsO}_4$  bending mode. The observation of two bands for the lavendulans compared with a single band for lemanskiite indicates that the structures of the two minerals are different.

Other low wavenumber bands for the sampleite and its polymorph are observed at 356 and 383  $\text{cm}^{-1}$ . A likely assignment is to CuO stretching vibrations<sup>35-39</sup>. Vibrations in this position have been observed and assigned to this vibration<sup>35-39</sup>. The observation of this mode at two different positions supports the fact that the two sampleite minerals have slightly different molecular structures. Two other bands are observed at 282 and 224  $\text{cm}^{-1}$  for the sampleite polymorph from Victoria and at 289 and 221  $\text{cm}^{-1}$  for sampleite. Bands are also observed at around 190 and 172  $\text{cm}^{-1}$  attributed to CuCl stretching vibrations<sup>40-45</sup>. It is possible that longitudinal and transverse optic vibrations are observed in these minerals. It is probable that the band around 224  $\text{cm}^{-1}$  is the longitudinal optic vibration and the band at 190  $\text{cm}^{-1}$  is the transverse optic vibration<sup>26,27</sup>. More detailed studies are required to prove this concept. For lemanskiite a sharp band is observed at 220  $\text{cm}^{-1}$  with other low intensity bands at 280, 262 and 243  $\text{cm}^{-1}$ . The 220  $\text{cm}^{-1}$  band is common to the Raman spectra of the entire sampleite mineral group. For the lavendulan samples, Raman spectra show peaks at around 227  $\text{cm}^{-1}$ . A band is observed at around 178  $\text{cm}^{-1}$ . These bands are attributed to CuCl stretching vibrations. Both sampleite and lavendulan are centrosymmetric ( $P2_1/n$ ). For the minerals lemanskiite and zdenekite these bands may be assigned to TO/LO splitting. In the 77 K spectrum of lavendulan two well resolved peaks at 227 and 209  $\text{cm}^{-1}$  are obtained. The bands are very sharp with bandwidths of 12.2 and 9.8  $\text{cm}^{-1}$ .

## CONCLUSIONS

Raman spectroscopy has been used to characterise the sampleite mineral group namely sampleite ( $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ ), lavendulan ( $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ ), zdenekite ( $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ ), and the polymorph of lavendulan known as lemanskiite. The minerals are characterised by the spectroscopy of the two anions present in the structure either phosphate in the case of sampleite or arsenate in the case of zdenekite, lavendulan and lemanskiite. The  $\text{PO}_4$  stretching vibrations are found at high wavenumbers compared with many phosphate minerals. This reflects the strength of the bonding of the phosphate anion to the copper atom. Differences are observed in the Raman spectra of the polymorph from Victoria and sampleite from New South Wales. It is suggested that subtle differences exist in the structure of these two sampleites. For the arsenate anion based minerals, the most intense band is observed at around 854  $\text{cm}^{-1}$ . Differences are observed in the Raman spectrum between lavendulan and lemanskiite suggesting the structures of the two minerals are different. Differences are observed in the Raman spectrum between lavendulan and lemanskiite in line with the structures of the two minerals being different. Raman spectroscopy is a useful tool for distinguishing members of the sampleite group.



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Mineral	Formula	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\beta$ /°	Space Group	Z
Unnamed <sup>a</sup>	NaCaCu <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> Cl.5H <sub>2</sub> O	9.695(2)	9.673(2)	19.739(4)	102.61(3)	<i>P</i> 2 <sub>1</sub> / <i>c</i>	4
Sampleite <sup>b</sup>	NaCaCu <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> Cl.5H <sub>2</sub> O	9.676(2)	19.284(4)	9.766(2)	90.07(1)	<i>P</i> 2 <sub>1</sub> / <i>n</i>	4
Lavendulan <sup>c</sup>	NaCaCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl.5H <sub>2</sub> O	10.011(1)	19.478(2)	10.056(1)	90.37(1)	<i>P</i> 2 <sub>1</sub> / <i>n</i>	4
Lemanskiite <sup>d</sup>	NaCaCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl.5H <sub>2</sub> O	10.0156(1)		36.691(3)		<i>P</i> 4 <sub>1</sub> 22	8
Zdenekite <sup>e</sup>	NaPbCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl.5H <sub>2</sub> O	10.023(7)	19.55(1)	10.023(6)	90.02(1)	<i>P</i> 2 <sub>1</sub> / <i>c</i>	8

<sup>a</sup>Lake Boga, Victoria, Australia. <sup>b</sup>Northparkes mine, Goonumbla, New South Wales, Australia. <sup>c</sup>Laurion, Greece. <sup>d</sup>El Guanaco mine, Station East Catalina, Chile; enantiomorphous space group *P*4<sub>3</sub>22 equally probable; no single-crystal data, cell refined from powder diffraction data and space group supposedly assigned by analogy to zdenekite<sup>22,23</sup>. <sup>e</sup>Cap Garonne mine, Var, France; enantiomorphous space group *P*4<sub>3</sub>22 equally probable; cell derived from single-crystal X-ray study (precession camera) but a single-crystal structure was not carried out. The only unknown structure is that of lemanskiite. A new lemanskiite mineral has been found.<sup>1</sup>

**Table 1 Unit cell data for the sampleite group**

<b>Sampleite</b>	<b>Lavendulan</b>	<b>Lemanskiite</b>	<b>Zdenekite</b>	<b>Suggested band assignments</b>
3567	3563	3559		OH stretching of water
3519	3529	3515	3483	OH stretching of water
	3433	3445	3443	OH stretching of water
3314	3346	3315	3360	OH stretching of water
3166	3296	3194	3108	OH stretching of water
	3220			OH stretching of water
2908	3040	2988	2927	OH stretching of water
	2176	2186		Overtone
		2033		Overtone
1645	1644		1637	Water HOH bending
	1629			Water HOH bending
1616	1616	1618		Water HOH bending
1542	1584	1560		
			1400	
1171	1207	1188	1194	
1148	1112	1118	1114	
1102		1061	1075	
1066			1074	PO <sub>4</sub> antisymmetric stretching mode
1037			1033	
995		981	1002	
957	922	921	938	PO <sub>4</sub> symmetric stretching mode
	884	886	912	
	861	862	850	AsO <sub>4</sub> antisymmetric stretching mode
	836	834	838	
	814			
789	784	784	767	Water librational mode
620	764	722		AsO <sub>4</sub> symmetric stretching mode
	643	634		
		606		

**Table 2 Results of the band component analysis of the infrared spectra of sampleite, lavendulan, lemanskiite and zdenekite**

**Table 3. Raman spectroscopic analysis of the sampleite group of minerals**

Sampleite NSW	Sampleite Vic	Zdenekite	Zdenekite (France)	Lemanskiite	Lavendulan WA		Lavendulan SA		Suggested assignment
298 K	298 K	298 K	298 K	298 K	298 K	77 K	298 K	77 K	
1269 1152 1088 1016	1264 1160 1087	1261 1171 1075 1012	1109	1369 1264 1165	1053	1053	1057	1049	(v <sub>3</sub> ) PO <sub>4</sub> antisymmetr ic stretching mode
997 962 924	997 960		936		981	981	976	925	(v <sub>1</sub> ) PO <sub>4</sub> symmetric stretching mode
		879 855	850 795	910 878 853 800 775	893 878 856 783	891 878 856 809	878 853	891 858 805	AsO <sub>4</sub> stretching modes
643 604 591 557	639 588 548	646 546 525	537	545	614 543	613 544	615 544	606 545 476	PO <sub>4</sub> bending mode
455 356	451 383 347	482 428 332	486 445 339	479 440 400 345	406 342	410 336	407 342	413 338	PO <sub>4</sub> / AsO <sub>4</sub> bending modes
282	289	261	278	280	278	273	278	274	

224	221	232	247	262	226	227	226	227	
190	187	204		243	176	209			
172	157	155		220		178			
		125		172					

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Figure 1 SEM images of (a) sampleite (b) lavendulan (c) lemanskiite (d) zdenekite

Figure 2 Infrared spectra of the hydroxyl stretching region of (a) sampleite (b) lavendulan (c) lemanskiite (d) zdenekite

Figure 3 Infrared spectra of the water deformation region of (a) sampleite (b) lavendulan (c) lemanskiite (d) zdenekite

Figure 4 Infrared spectra of the low wavenumber region of (a) sampleite (b) lavendulan (c) lemanskiite (d) zdenekite

Figure 5 Raman spectra of the 700 to 1200  $\text{cm}^{-1}$  region of (a) sampleite (Victoria) (b) sampleite (NSW) (c) lemanskiite (d) lavendulan (WA) (e) lavendulan (SA) (f) zdenekite (Australia) (g) zdenekite (France)

Figure 6 Raman spectra of the 200 to 700  $\text{cm}^{-1}$  region of (a) sampleite (Victoria) (b) sampleite (NSW) (c) lemanskiite (d) lavendulan (WA) (e) lavendulan (SA) (f) zdenekite (Australia) (g) zdenekite (France)

Figure 7 Raman spectrum of lavendulan at 298 and 77 K.

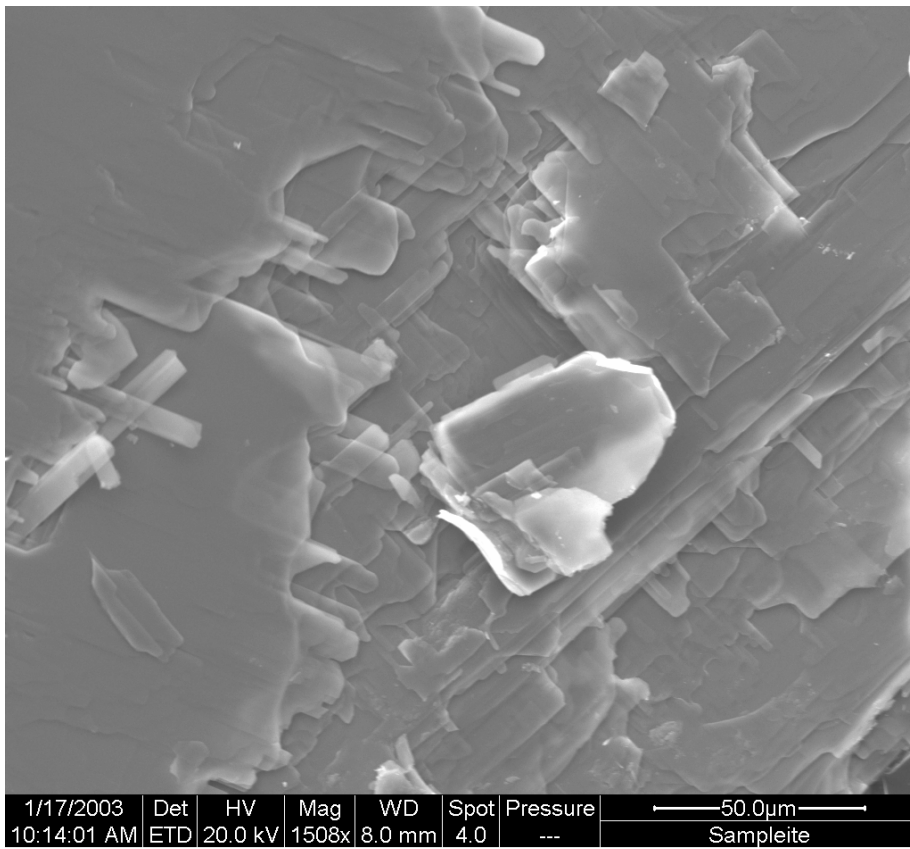
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Table 1. X-ray diffraction of the sampleite mineral group

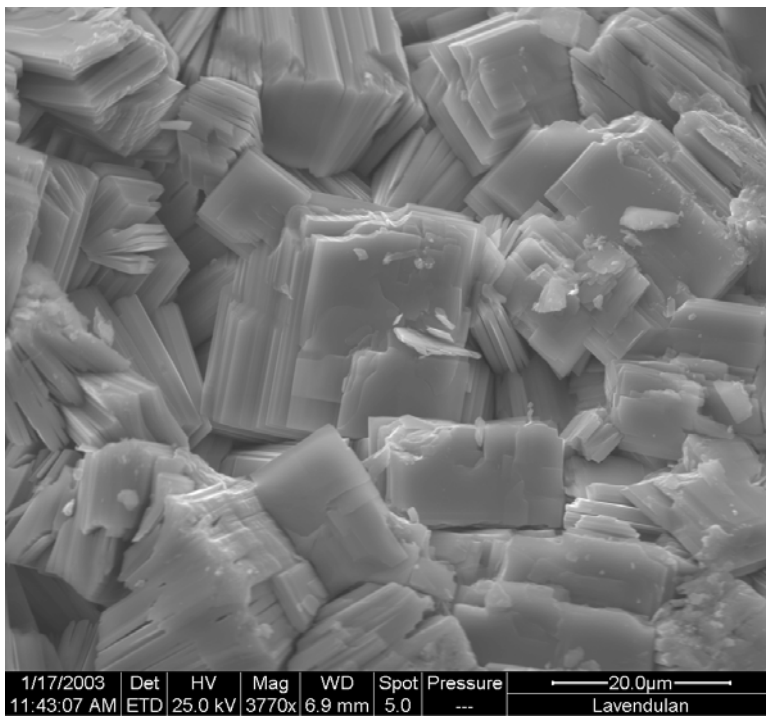
Table 2. Results of the band component analysis of the infrared spectra of sampleite, lavendulan, lemanskiite and zdenekite

Table 3. Raman spectroscopic analysis of the sampleite group of minerals

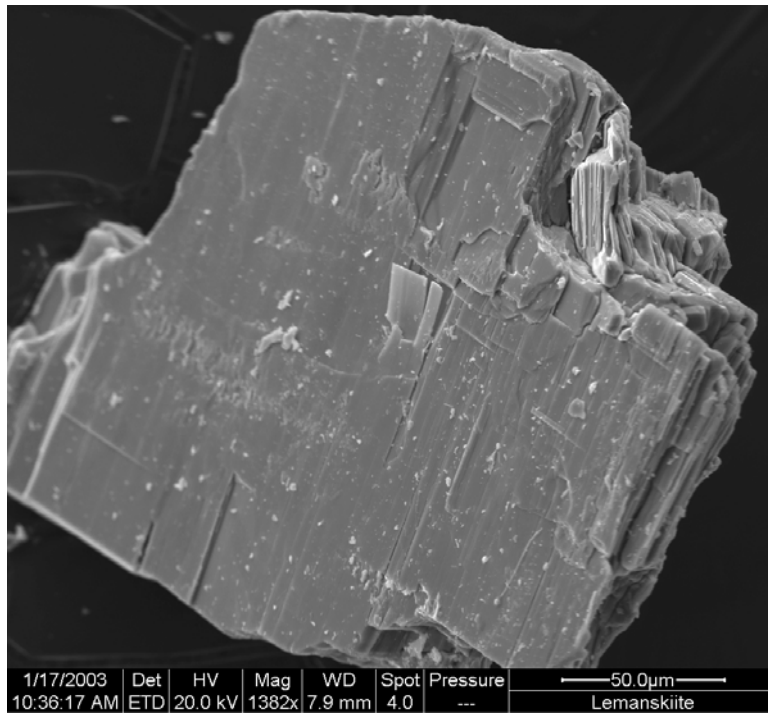




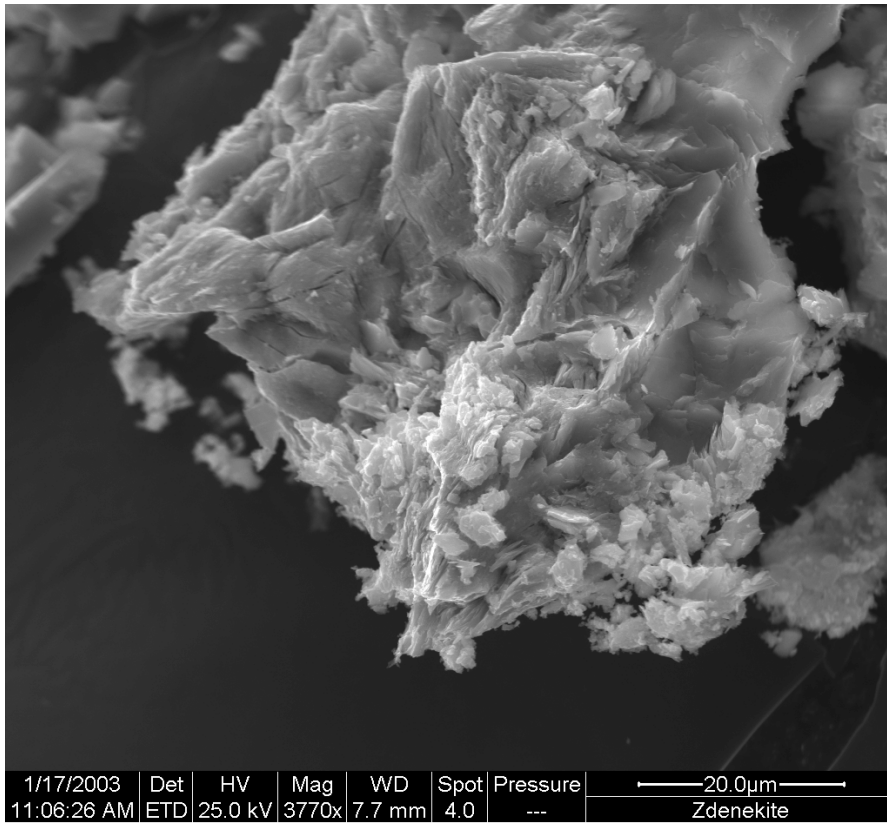
**Figure 1a**



**Figure 1b**



**Figure 1c**



**Figure 1d**

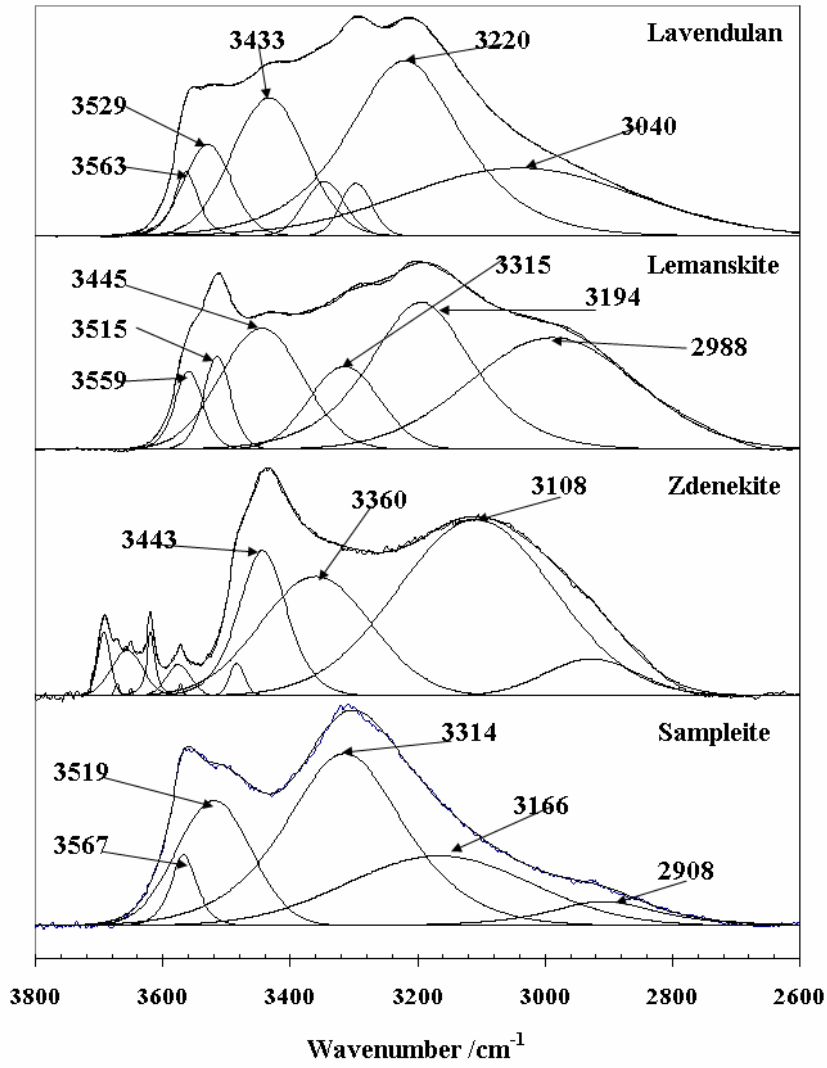
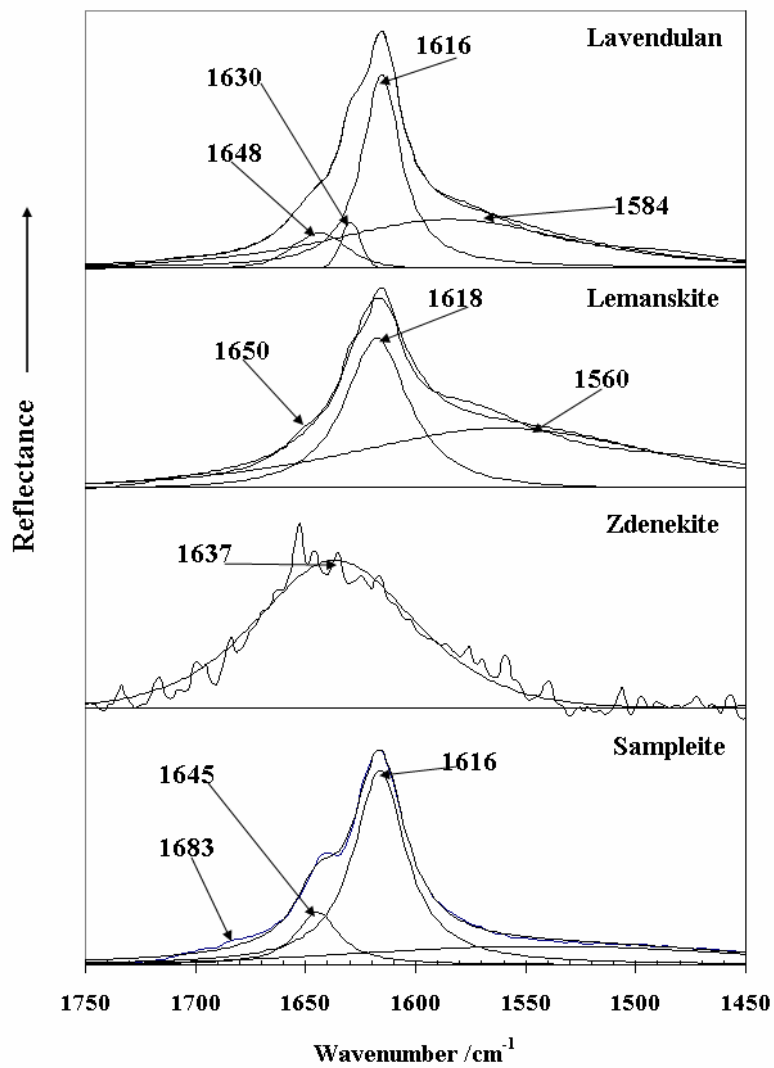


Figure 2



**Figure 3**

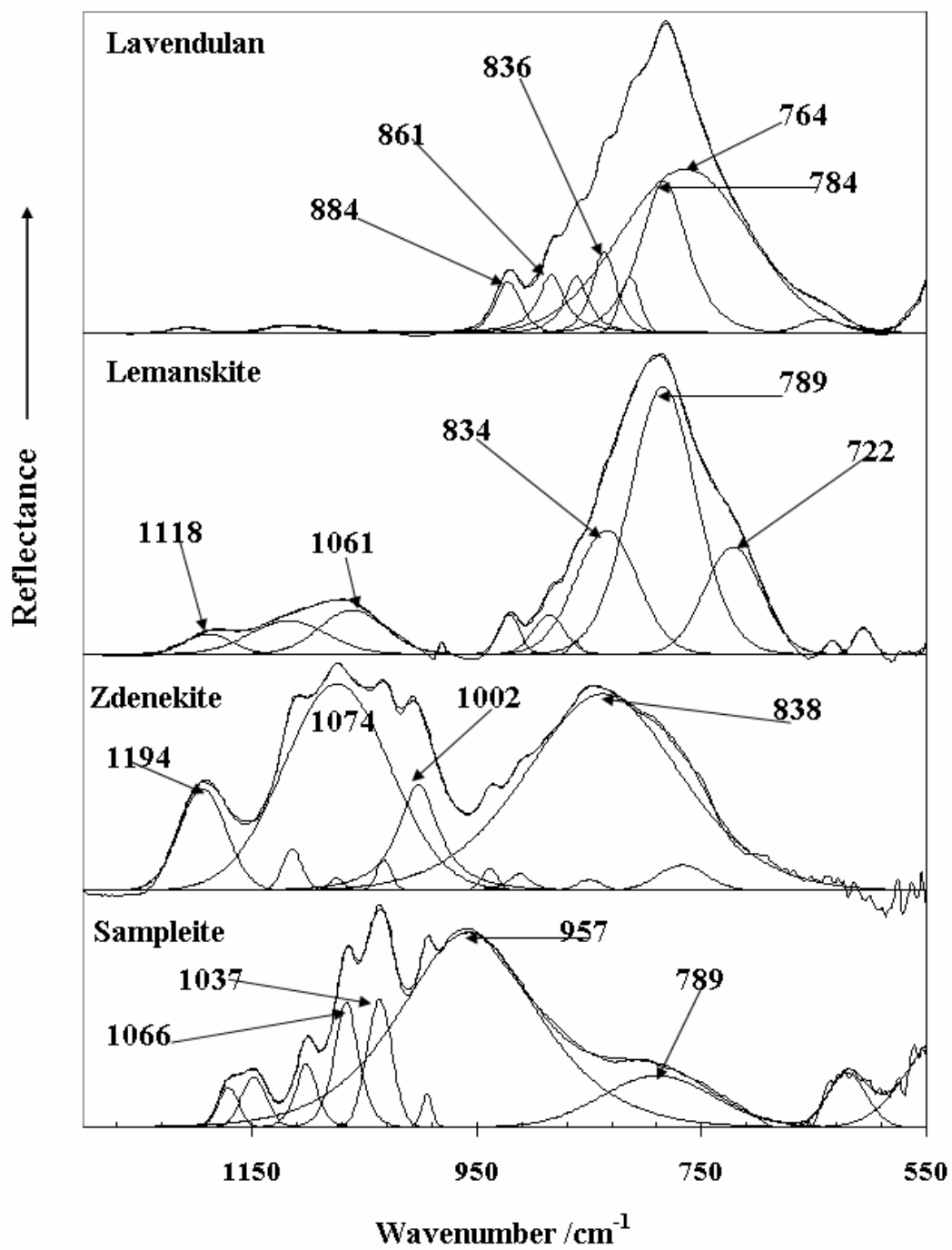


Figure 4

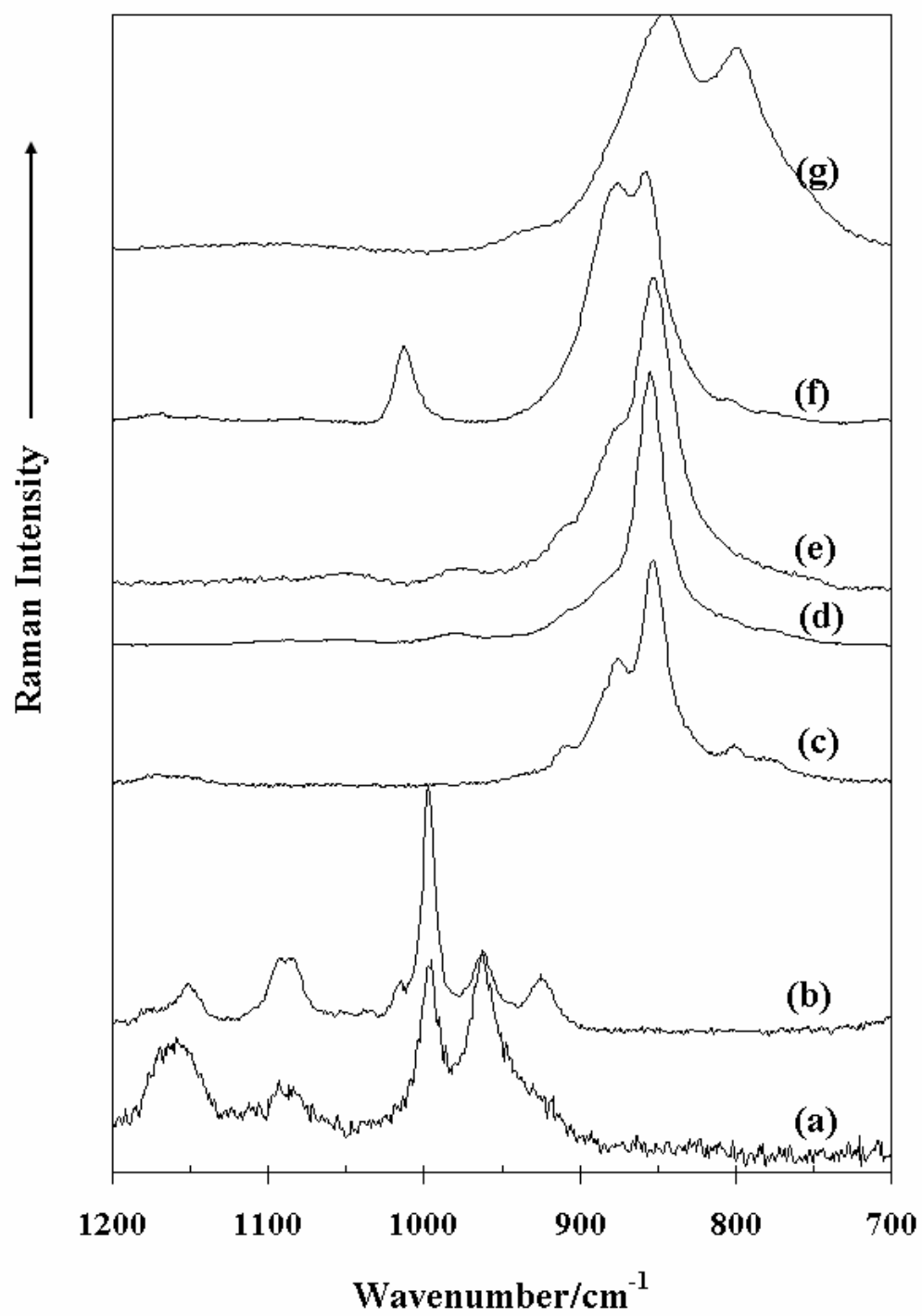
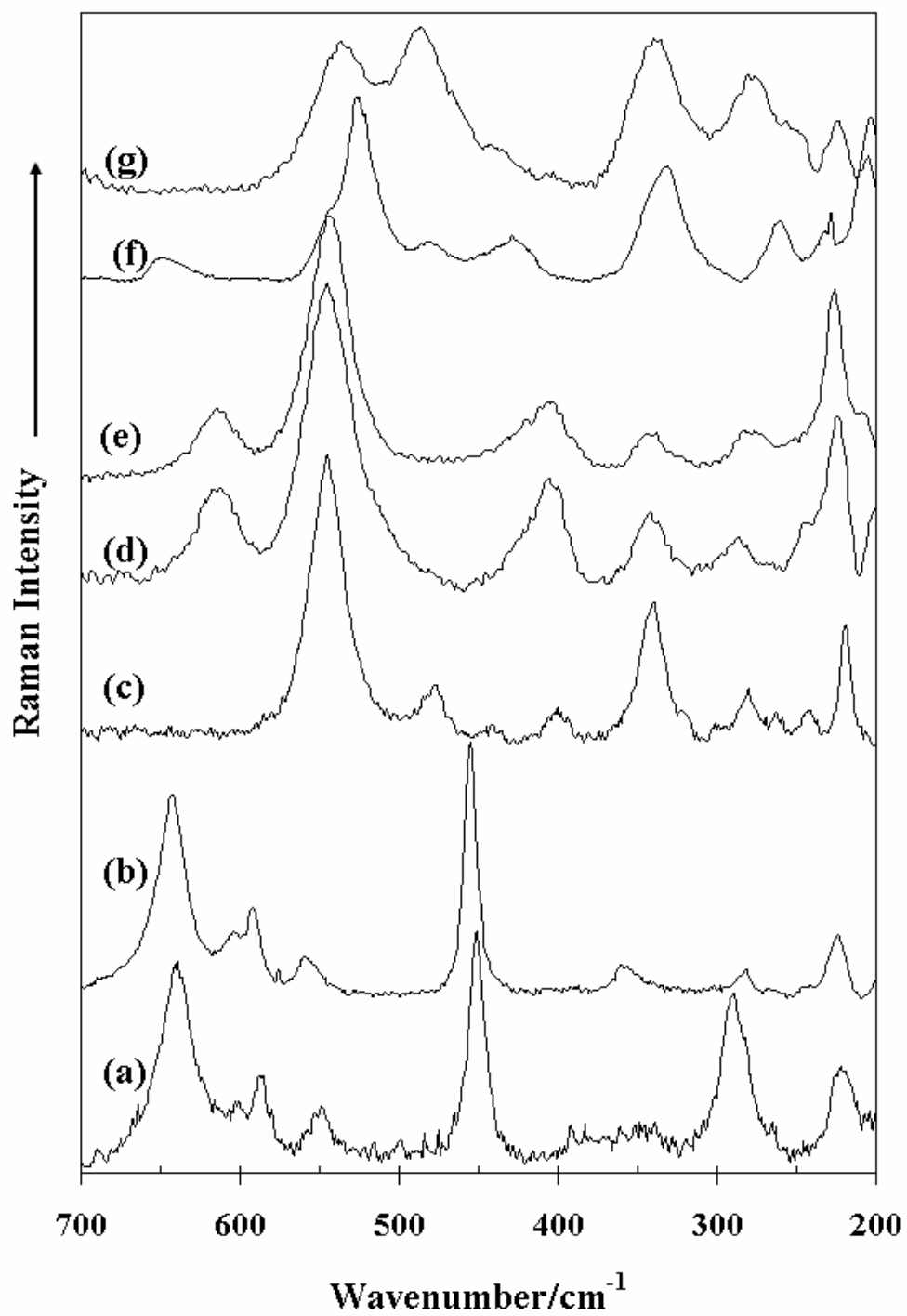


Figure 5



**Figure 6**



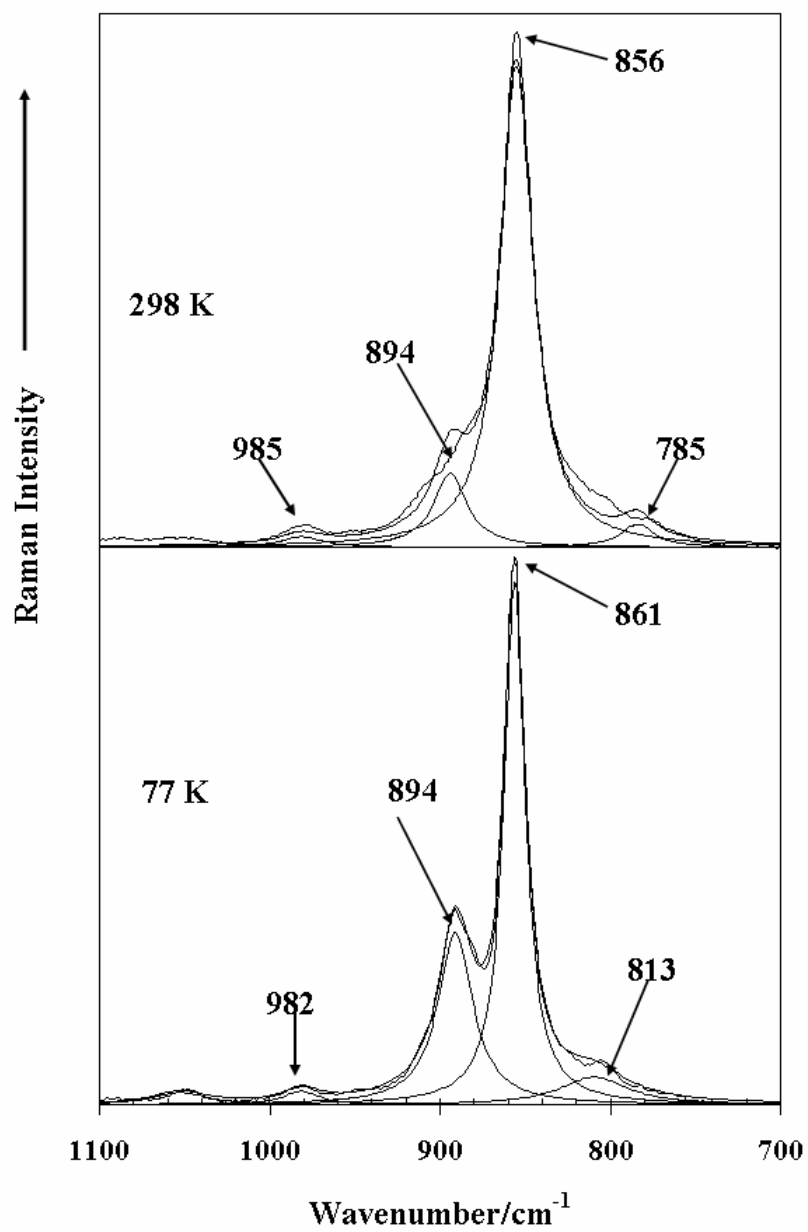


Figure 7