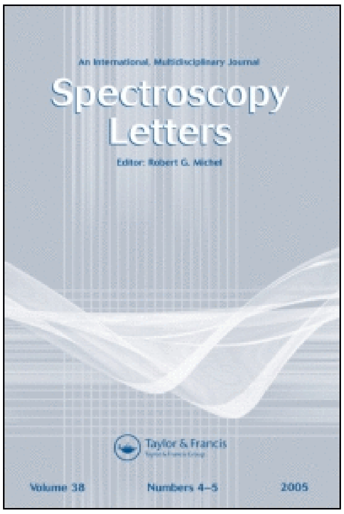

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Ray L. Frost[a]; Silmarilly Bahfenne[a]
[a] Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland, Australia

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The Mineral Nealite $Pb_4Fe^{2+}(AsO_3)_2Cl_4 \cdot 2H_2O$—A Raman Spectroscopic Study

Ray L. Frost,
and Silmarilly Bahfenne
Chemistry Discipline, Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland, Australia

ABSTRACT The mineral nealite $Pb_4Fe^{2+}(AsO_3)_2Cl_4 \cdot 2H_2O$ is of archaeological significance as it is man made mineral formed through the dumping of mine wastes in the sea. The mineral has been studied by Raman spectroscopy. Raman spectroscopy identifies intense Raman bands at 708 and 732 cm^{-1} assigned to AsO_3^{3-} stretching vibrations. In addition low intensity bands are observed at 604 and 632 cm^{-1}, which are attributed to $As_2O_4^{2-}$ symmetric and antisymmetric stretching modes. Low intensity Raman band is observed at 831 cm^{-1} and is assigned to the AsO_4^{4-} stretching vibration. Intense Raman bands at 149 and 183 cm^{-1} are attributed to M-Cl stretching vibrations. Raman spectroscopy identifies arsenic anions in different oxidation states in the mineral. The molecular structure of the mineral nealite, as indicated by Raman spectroscopy, is more complex than has been reported by previous studies.

KEYWORDS archaeology, arsenite, nealite, Raman spectroscopy

INTRODUCTION

The mineral nealite $Pb_4Fe^{2+}(AsO_3)_2Cl_4 \cdot 2H_2O$[1] is found at the ancient mine site of Laurion or Laurium, Greece.[2–4] The mine sites date from the 7th century BC. (See for example http://us.geocities.com/classicalbackpacking/thorikos.html). The mineral was first discovered in 1980 by Dunn and Rouse.[5] The mineral was formed in the slag dumps from this ancient mine site through the dumping of mine waste in the sea.[3,6] The mineral has been found at other sites.[4] It is open to question whether the compound is a 'natural' mineral or not because it was formed through the hands of man. The mineral, however, has been listed by the IMA (International Mineralogical Association) and is yellow to a reddish orange in colour with large prismatic crystals and the mineral is triclinic.[7] The cell dimensions are $a = 6.537$, $b = 10.239$, $c = 5.588$, $Z = 1$; alpha $= 96.2°$, beta $= 89.39°$, gamma $= 97.74°$ $V = 368.42$. The crystal system is Triclinic-PinacoidalH-M Symbol (1) Space Group: P1.[7]

Interest in arsenates and arsenites stems from their use as poisons and toxic chemicals and their formation in slag dumps and old mine sites.[8–10]

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Address correspondence to Ray L. Frost, Chemistry Discipline, Faculty of Science and Technology, 2 George Street, P.O. Box 2434 GPO, Brisbane 4001, Australia. E-mail: r.frost@qut.edu.au

There have been some studies using both infrared and Raman spectroscopy of arsenite containing minerals.[9,11–13] Most of these studies involve aqueous systems.[9] Indeed the stability of many arsenite compounds in aqueous media is questioned.[9] However the mineral nealite is formed in seawater and consequently must be stable in water. Of course band positions identified in aqueous systems might not be the same as in the solid state or for arsenite containing minerals such as nealite. Bencivenni and Gingerich based upon matrix isolated studies identified the band positions of AsO_3 for a range of arsenite containing compounds.[14] Infrared bands in the 763 to 868 cm^{-1} region were identified as the symmetric stretching bands; bands in the 743 to 853 cm^{-1} in positions lower in wavenumbers to the symmetric stretching modes were classified as the antisymmetric stretching vibrations. The position of the bending mode varied from 330 to 418 cm^{-1}.

It is interesting to note that very few papers have been published on the spectroscopy of arsenite minerals. What research has been published is related to the analysis of pigments.[15–17] Very few studies of related minerals such as mineral arsenites have not been undertaken using vibrational spectroscopy,[18–20] even though Raman spectroscopy has proven especially useful for the study of minerals.[21–29] Very few spectroscopic studies of the mineral nealite have been undertaken, yet such studies would be very useful for determination of minerals of archaeological significance. It is noted that a Raman spectrum of nealite is provided in the RRUFF data base [http://rruff.info/nealite/display=default/]. Two spectra are given but are very different. This research sets out to determine which is the correct spectrum of nealite.

The aim of this paper is to report the Raman spectra of nealite and to relate the spectra to the crystal chemistry and formula of this pseudo-mineral. This paper follows the systematic research on Raman and infrared spectroscopy of secondary minerals containing oxy-anions formed in the oxidation zone of minerals.

EXPERIMENTAL

Minerals

The mineral nealite was obtained from the Mineralogical Research Company. The mineral originated from Laurion, Attica, Greece. The composition of the mineral has been published.[1]

Raman Spectroscopy

Crystals of nealite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50×) 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. Power at the sample was 0.2 mW. Spectra were obtained from different crystals and were compared for consistency. The composition of the mineral is well defined and homogenous and did not affect the Raman spectrum. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed 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 Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

RESULTS AND DISCUSSION

The Raman spectrum of nealite in the 500 to 1100 cm^{-1} region is shown in Fig. 1. Two intense bands are observed at 708 and 732 cm^{-1} and are

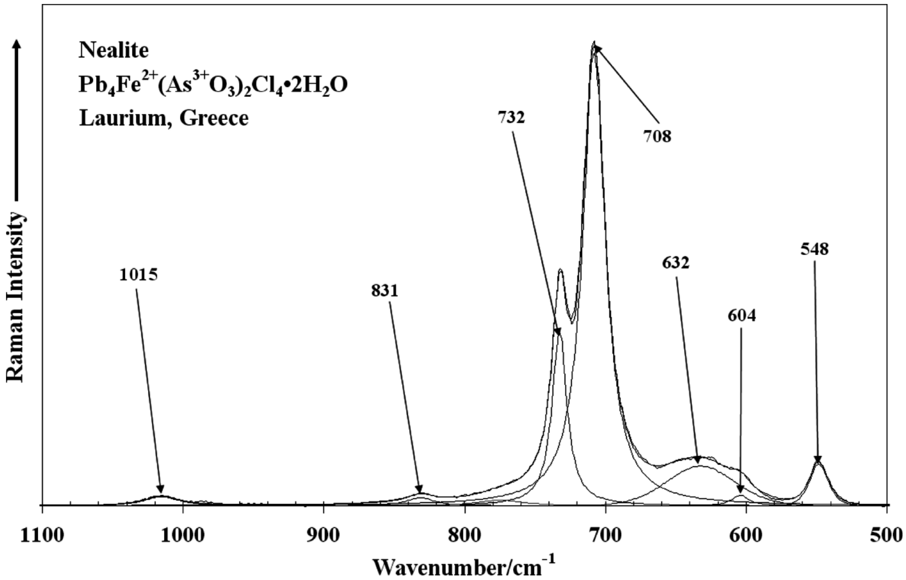

FIGURE 1 Raman spectrum of nealite in the 500 to 1100 cm^{-1} region.

assigned to the AsO_3^{3-} ν_1 symmetric stretching and ν_3 antisymmetric stretching vibrations. Raman bands of lower intensity are observed at 548, 604, and 632 cm^{-1}. The latter two bands are broad. Bands in similar positions are observed for minerals such as leiteite, an arsenite mineral with $(As_2O_4)^{2-}$ units (Frost and Bahfenne, in press). Two low intensity Raman bands for leiteite are found at 600 and 647 cm^{-1} and assigned to the $(As_2O_4)^{2-}$ antisymmetric stretching vibrations of AsO_2 units. Ogden and Williams[30] published the infrared spectra of selected arsenite compounds and observed bands at 393, 852 and 863 cm^{-1}. The latter two bands were assigned to the $(As_2O_4)^{2-}$ stretching vibrations. Bencivenni and Gingerich reported the infrared spectra of matrix isolated synthetic $NaAsO_2$, $KAsO_2$, $RbAsO_2$, and $CsAsO_2$.[14] All the spectra of the isolated matrix showed bands at 868, 853, and 418 cm^{-1}. These authors assigned these bands to the $(AsO_2)^-$ symmetric stretching vibration, antisymmetric stretching vibration and the symmetric bending mode.[14] These authors noted that the position of the symmetric stretching vibration occurred at higher wavenumbers than the antisymmetric stretching vibration which is unusual for the vibrational spectroscopy of oxyanions.[14] Szymanski et al.[9] reported the infrared and Raman spectra of M_3AsO_3 metal arsenites. An intense Raman band was observed at 670 cm^{-1} and an intense band in the infrared spectrum at 560 cm^{-1}. A very low intensity band is observed at 831 cm^{-1} and is attributed to the AsO_4^{4-} ν_1 symmetric stretching mode. The presence of this band provides evidence for the oxidation of the arsenite anion to the arsenate anion. A second low intensity band is observed at 1015 cm^{-1}. This band may be attributed to a SO_4^{2-} symmetric stretching mode. The presence of this vibration may indicate the presence of sulphate at low amounts in the mineral or alternatively a second mineral phase is present in the analysis. However this latter conclusion seems unlikely as the spatial resolution of the instrument is around 1 micron or less and the crystals of nealite are quite large.

The Raman spectrum of the low wavenumber region from 100 to 500 cm^{-1} is displayed in Fig. 2. An intense band is observed at 320 cm^{-1} with component bands at 299 and 342 cm^{-1}. A second moderately intense band is observed at 393 cm^{-1}. The likely assignment of the first set of bands is assigned to the ν_4 $(AsO_3)^{3-}$ bending modes and the band at 393 cm^{-1} to the ν_2 $(AsO_3)^{3-}$ bending mode. A Raman band is observed at 471 cm^{-1}. This band is assigned to the ν_2 $(As_2O_4)^{2-}$ bending mode. This band may correspond to the infrared band observed by Ogden and Williams at 393 cm^{-1}. Szymanski et al.[9] also found a Raman band at 375 cm^{-1}. Bencivenni and Gingerich found a band at 418 cm^{-1} and assigned this band to the δ AsO_2 bending mode.[14] Intense Raman bands are observed at 149 cm^{-1} with shoulder bands at 137

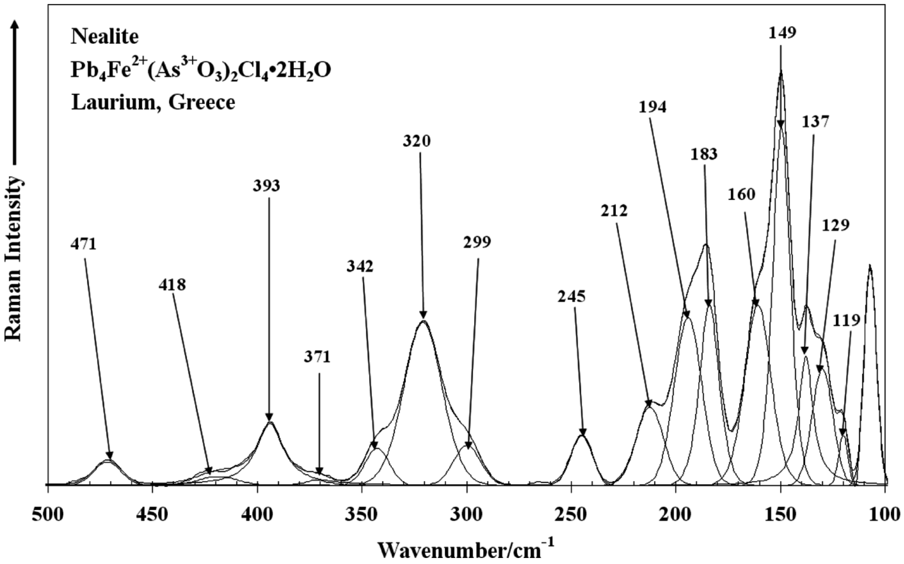

FIGURE 2 Raman spectrum of nealite in the 100 to 500 cm^{-1} region.

and 160 cm^{-1}. Raman bands are also observed at 183 and 194 cm^{-1}. One possible assignment of these bands is to PbCl and FeCl stretching vibrations. Bands in similar positions have been observed for other minerals of archaeological significance including blixite, boleite, cumengeite, diaboleite and laurionite.[31–33] The two sets of bands may be due to M-Cl longitudinal and transverse optical vibrations. The Raman spectrum of the compound iron hydroxychloride β-$Fe_2(OH)_3Cl$ shows bands in similar positions. Such a compound is of archaeological significance.[34] Reguer et al.[34] identified bands at 127, 160, 200, and 318 cm^{-1}. The bands for β-$Fe_2(OH)_3Cl$ are in harmony with the Raman bands for nealite.

It is noted that there are no Raman bands of any intensity in the 1100 to 2700 cm^{-1} range. The Raman spectrum of nealite in the 2700 to 3500 cm^{-1} region is reported in Fig. 3. The Raman spectrum is complex with a significant number of bands. Raman bands are observed at 3215, 3357, 3387, 3431, and 3451 cm^{-1}. Broad low intensity bands are observed at 2849 and 2892 cm^{-1}. These bands are attributed to organic compounds perhaps adsorbed on the mineral

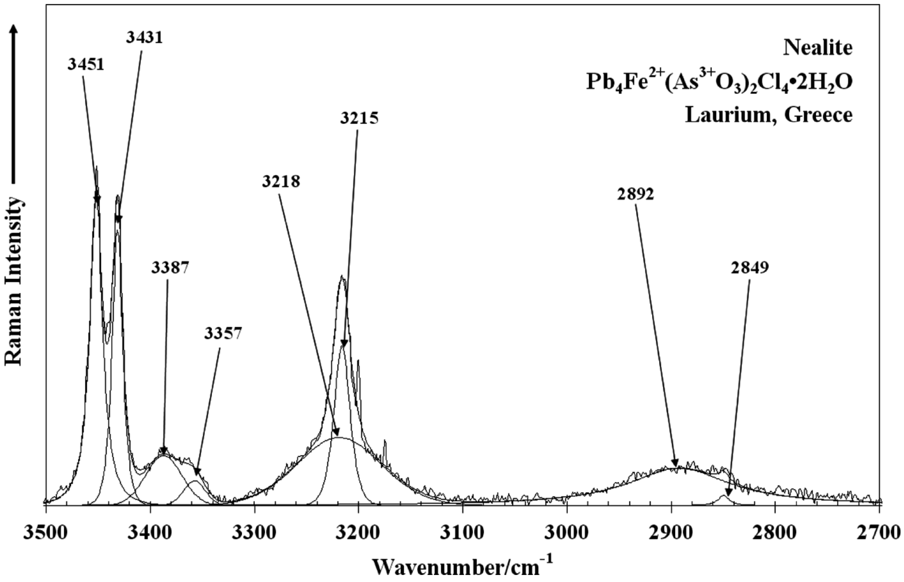

FIGURE 3 Raman spectrum of nealite in the 2700 to 3500 cm^{-1} region.

surface. The Raman bands in the 3200 to 3500 cm^{-1} region are attributed to water stretching vibrations. The structure of the mineral[7] is such that water is coordinated to both Pb^{2+} and Fe^{2+} in a number of energy states resulting in different bond distances which thus give Raman bands in different positions.

CONCLUSIONS

The mineral nealite is one of those minerals of archaeological significance. The mineral is formed through the dumping of mine wastes into the sea. The Raman spectrum of the mineral nealite has been obtained for the first time and the spectra are related to the molecular structure of the mineral. The Raman spectrum is complex with Raman bands attributed to $(AsO_3)^{3-}$, $(As_2O_4)^{2-}$, and AsO_4^{4-} units, showing arsenic in different oxidation states. Thus this observation shows the molecular structure of nealite is more complex than has been indicated in the literature. This complexity is confirmed by the number and position of bands in the OH stretching region ascribed to water in different molecular environments.

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REFERENCES

1. Pertlik, F.; Schnorrer, G. *Mineral. Petrol.* **1993**, *48*, 193–200.
2. Jaxel, R.; Gelaude, P. *Mineral. Rec.* **1986**, *17*, 183–190.
3. Rewitzer, C.; Hochleitner, R. *Rivista Mineral. Italiana* **1989**, 83–100.
4. Schnorrer-Koehler, G. *Aufschluss* **1987**, *38*, 291–300.
5. Dunn, P. J.; Rouse, R. C. *Mineral. Rec.* **1980**, *11*, 299–301.
6. Palenzona, A.; Bulgarelli, G.; Ciriotti, M.; Selmi, P. *Rivista Mineral. Italiana* **1998**, 39–41.
7. Giuseppetti, G.; Mazzi, F.; Tadini, C. *Neues Jahrbuch Mineralogie, Monatshefte* **1993**, 278–288.
8. Beilina, A. Z.; Zhambekov, M. I.; Zhumanova, K. M.; Isabaev, S. M.; Muldakhmetov, Z. M. Vibrational spectra of some sodium arsenates and their thio salts. Khim.-Metall. Inst., Karaganda, USSR., 1974, p. 15
9. Szymanski, H. A.; Marabella, L.; Hoke, J.; Harter, J. *Appl. Spectrosc.* **1968**, *22*, 297–304.
10. Wilcox, D. E.; Bostick, B. C.; Gehrke, G. E.; Spuches, A. M.; Quinn, C. F. Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25–29, 2007, INOR, 2007, 435.
11. Ghosh, J. C.; Das, S. K. *J. Phys. Chem.* **1932**, *36*, 586–594.
12. Loehr, T. M.; Plane, R. A. *Inorg. Chem.* **1968**, *7*, 1708–1714.
13. Wood, S. A.; Tait, C. D.; Janecky, D. R. *Water-Rock Interact., Proc. Int. Symp.*, 9th; 1998; 863–866.
14. Bencivenni, L.; Gingerich, K. A. *J. Mol. Struct.* **1983**, *99*, 23–29.
15. Correia, A. M.; Oliveira, M. J. V.; Clark, R. J. H.; Ribeiro, M. I.; Duarte, M. L. *Anal. Chem.* (Washington, DC, United States) **2008**, *80*, 1482–1492.
16. Correia, A. M.; Clark, R. J. H.; Ribeiro, M. I. M.; Duarte, M. L. T. S. *J. Raman Spectros.* **2007**, *38*, 1390–1405.
17. Clark, R. J. H.; Cridland, L.; Kariuki, B. M.; Harris, K. D. M.; Withnall, R. *J. Chem. Soc., Dalton Trans.: Inorg. Chem.* **1995**, 2577–2582.
18. Paques-Ledent, M. T.; Tarte, P. *Spectrochim. Acta, Part A* **1974**, *30A*, 673–689.
19. Gevork'yan, S. V.; Povarennykh, A. S. *Konst. Svoistva Miner.* **1975**, *9*, 73–81.
20. Braithwaite, R. S. W. *Mineral. Mag.* **1983**, *47*, 51–57.
21. Frost, R. L.; Cejka, J.; Ayoko, G. *J. Raman Spectrosc.* **2008**, *39*, 495–502.
22. Frost, R. L.; Cejka, J.; Ayoko, G. A.; Dickfos, M. J. *J. Raman Spectrosc.* **2008**, *39*, 374–379.
23. Frost, R. L.; Cejka, J.; Dickfos, M. J. *J. Raman Spectrosc.* **2008**, *39*, 779–785.
24. Frost, R. L.; Dickfos, M. J.; Cejka, J. *J. Raman Spectrosc.* **2008**, *39*, 582–586.
25. Frost, R. L.; Hales, M. C.; Wain, D. L. *J. Raman Spectrosc.* **2008**, *39*, 108–114.
26. Frost, R. L.; Keeffe, E. C. *J. Raman Spectrosc.* **2008**.
27. Frost, R. L.; Locke, A.; Martens, W. N. *J. Raman Spectrosc.* **2008**, *39*, 901–908.
28. Frost, R. L.; Reddy, B. J.; Dickfos, M. J. *J. Raman Spectrosc.* **2008**, *39*, 909–913.
29. Palmer, S. J.; Frost, R. L.; Ayoko, G.; Nguyen, T. *J. Raman Spectrosc.* **2008**, *39*, 395–401.
30. Odgen, J. S.; Williams, S. J. *J. Mole. Structure* **1982**, *80*, 105–108.
31. Frost, R. L.; Kloprogge, J. T.; Williams, P. A. *Neues Jahrbuch Mineralogie, Monatshefte* **2003**, 529–542.
32. Frost, R. L.; Martens, W.; Kloprogge, J. T.; Ding, Z. *Spectrochimica Acta, Part A: Mol. Biomol. Spectrosc.* **2003**, *59A*, 2705–2711.
33. Frost, R. L.; Williams, P. A.; Martens, W. *Mineral. Maga.* **2003**, *67*, 103–111.
34. Reguer, S.; Neff, D.; Bellot-Gurlet, L.; Dillmann, P. *J. Raman Spectrosc.* **2007**, *38*, 389–397.