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Raman spectroscopy of the copper chloride minerals nantokite, eriochalcite and claringbullite –implications for copper corrosion

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Abstract

The application of Raman spectroscopy to the study of the copper chloride minerals nantokite, eriochalcite and claringbullite has enabled the vibrational modes for the CuCl, CuOH and CuOH₂ to be determined. Nantokite is characterised by bands at 205 and 155 cm⁻¹ attributed to the transverse and longitudinal optic vibrations. Nantokite also has an intense band at 463 cm⁻¹, eriochalcite at 405 and 390 cm⁻¹ and claringbullite at 511 cm⁻¹. These bands are attributed to CuO stretching modes. Water librational bands at around 672 cm⁻¹ for eriochalcite have been identified and hydroxyl deformation modes of claringbullite at 970, 906 and 815 cm⁻¹ are observed. Spectra of the three minerals are so characteristically different that the minerals are readily identified by Raman spectroscopy. The minerals are often determined in copper corrosion products by X-ray diffraction. Raman spectroscopy offers a rapid, in-situ technique for the identification of these corrosion products.

Key Words- copper, chloride, Raman spectroscopy, nantokite, eriochalcite and claringbullite

INTRODUCTION

Studies of copper chlorides have been undertaken over a long period of time. (BRALY, A., 1923; LACROIX, A., 1907) Such studies have two aspects namely the corrosion of metallic copper (FALTERMEIER, R. B., 1999; KRATSCHMER, A. et al., 2002; NASSAU, K. et al., 1987; STRANDBERG, H. and JOHANSSON, L.-G., 1998; UMINSKI, M. and GUIDETTI, V., 1995) and secondly the study of copper artefacts of archaeological importance. (LACROIX, A., 1907; ORGAN, R. M., 1959; OTERO, E. et al., 1994; ZAYKOV, V. V. et al., 1999) Three stoichiometrically related minerals of interest in these studies are nantokite (CuCl), eriochalcite (CuCl₂·2H₂O) and claringbullite Cu₄Cl[Cl_{0.29}(OH)_{0.71}](OH)₆. (BURNS, P. C. et al., 1995) For example some metal objects found at a medieval site on St. Ninian's island, Shetland, showed extensive corrosion with cuprite (Cu₂O) and nantokite formation. (ORGAN, R. M., 1959) It remains questionable that such a mineral could be stable in a moist environment such as might be found at this location. Such minerals are found in the supergene deposits in arid climates such as in the Atacama province, Chile and elsewhere. (SEGERSTROM, K., 1967; SHARPE, J. L. and WILLIAMS, P. A., 1999)

Nantokite is named after the site of its discovery, Nantoko, Chile. The mineral is colourless to white and its crystal structure is cubic: space group F $\bar{4}3m$. It thus possesses a zinc-blende structure and has only one fundamental (T₂) active in both

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infrared and Raman spectra. Other bands are the result of impurities and multiphonon excitations. Eriochalcite is blue-green and has a crystal structure orthorhombic, space Group *Pbmn* (*P2/m*) *2/m 2/m*. (ENGBERG, A., 1970) The structure consists of planar, centrosymmetric molecules linked by weak intermolecular Cl→Cu interactions over long distances (2.94Å) and stacked in columns. (ENGBERG, A., 1970) Due to the symmetry and number of molecules in the unit cell ν_s (ClCuCl) (correlation and isotope splitting) and ν_s (OCuO) should be observed in the Raman spectra. In addition the in-plane deformation modes of gerade parity of the CuCl₂O₂ skeleton should be observed.

The crystal structure of claringbullite is hexagonal, *a* 6.6733(5), *c* 9.185(1) ° V 354.22(6) ° 3, *Z* = 2, space group $\overline{P}6_3/mmc$. (BURNS, P. C. et al., 1995; FEJER, E. E. et al., 1977) The structure consists of a three-dimensional network of non-equivalent, short Cu-OH bonds (from 1.95 to 1.99Å) between two different kinds of linked polyhedra. Cu...Cl distances are long and of the order of 3.0Å. The respective bonds are so weak that they will be of low wavenumbers and intensity. For both eriochalcite and claringbullite, the number of formula units in the unit cell is 2. There are 9 atoms in eriochalcite and 41 for claringbullite which implies a dynamic space dimension of 27 for eriochalcite and 123 for claringbullite. Hence this represents the number of vibrations which should be observed.

Nantokite is fundamentally cuprous chloride and is hygroscopic. It is a rare mineral and is isomorphous with miersite (AgI) and marshite (CuI). Eriochalcite is freely water-soluble and thus is confined to oxide zones in arid climates, as in the deposits of the Atacama Desert. Eriochalcite under the correct conditions can form more complex copper chloride minerals such as claringbullite. (FROST, R. L. et al., 2002) Other related minerals that can be formed in the presence of other anions such as sulphate and nitrate are connellite and buttgenbachite. (FROST, R. L. et al., 2002) If claringbullite is left in contact with the mother liquor then botallackite, atacamite and clinoatacamite, polymorphs of stoichiometry Cu₂Cl(OH)₃ can form. Each of these minerals is important both as a corrosion product and in the degradation of bronze and brass artefacts of antiquity. (NUNEZ, L. et al., 1998; OTERO, E. et al., 1994; SCOTT, D. A., 2000) Although many papers have been published on synthetic copper chloride minerals, (HONERLAGE, B. et al., 1977; KAMINOW, I. P. and TURNER, E. H., 1972; KRAUZMAN, M. et al., 1974; MURAHASHI, T. and KODA, T., 1976; NAGASAWA, N. et al., 1978; NEMANICH, R. J. and MIKKELSEN, J. C., JR., 1979) few papers have been published on the vibrational spectroscopy of the naturally occurring minerals. (FONTANA, P. and FABRI, G., 1957; HUNT, G. R. et al., 1972; POVARENENYKH, A. S., 1979; SCOTT, D. A., 2000) This may be because many of the bands relating to the CuCl and CuO vibrations occur below 400 cm⁻¹ and are therefore not easily measured using infrared spectroscopy. Further techniques such as infrared reflectance spectroscopy are also limited by the cut-off at even higher wavenumbers. Raman spectroscopy lends itself to the study of these types of minerals and to the best of our knowledge few, if any, Raman spectroscopic studies of these minerals have been forthcoming. In recent work by Bouchard, the Raman spectrum of a synthetic single copper chloride crystal was reported. (BOUCHARD-ABOUCACRA, M., 2001) In this work the longitudinal optic vibration was observed at 205 cm⁻¹ and the transverse optic vibration at 155 cm⁻¹. Combination modes were found at around 145 and 75 cm⁻¹. The spectrum of the natural nantokite mineral was not reported. Copper, brass and bronze

objects of archaeological, antiquarian and medieval significance have been studied by various techniques including the use of Raman spectroscopy. (ERDOS, E., 1968; HELMI, F. M. and ISKANDER, N. Y., 1985; KUCHITSU, N. et al., 1999; LACROIX, A., 1907; NUNEZ, L. et al., 1998; OTERO, E. et al., 1994; SELWYN, L. S. et al., 1996) Such a technique has been rightly proposed as imperative for the study of corroded bronze objects, in that it is non-destructive. (BOUCHARD-ABOUCACRA, M., 2001) Indeed, restoration of these types of objects can be aided by the application of Raman spectroscopy to the study of the degradation products formed on paintings of antiquity. (DEI, L. et al., 1998; KUCHITSU, N. et al., 1999; NAUMOVA, M. M. and PISAREVA, S. A., 1994; REIDERER, J., 1974)

EXPERIMENTAL

Minerals:

Nantokite and eriochalcite were obtained by one of the authors (PAW) from the Main Lode, Great Australia mine, Cloncurry, Queensland. Their structures were confirmed using powder X-ray methods. Eriochalcite was obtained from Atacama, Chile through the Mineral Research Co. Claringbullite was obtained from the Nchanga Open Pit, Chingola, Zambia and also from the M'sesa mine, Kambowe, Katanga (Shaba), Congo (Zaire). To obtain pure, non-hydrated nantokite, the matrix is broken open and the colourless to white mineral, which looks exactly like quartz is obtained. This newly exposed mineral is then analysed immediately, prior to oxidation and hydrolysis to form atacamite-group products.

Raman microprobe spectroscopy

The mineral samples were placed and oriented on the stage of an Olympus BSM microscope, equipped with 10x and 50x objectives. In the case of nantokite, a fresh sample was cleaved from the matrix to expose a fresh sample. In the case of claringbullite, the sample has a background matrix. The flat platy crystals were simply oriented under the microscope. The specimens were simply supported by plasticine to hold the mineral in place during analysis.

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). 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 100 and 4000 cm^{-1} . (FROST, R. L. et al., 2002)

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^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} . Infrared spectra of claringbullite were attempted using the diamond ATR cell and the micro-ATR cell without success. Spectroscopic calculations and manipulations were performed as previously described. (FROST, R. L. et al., 2002)

Results and Discussion

The reason for the selection of these three minerals for spectroscopic study is multifold. There is a compositional relationship between the three minerals and they are known to be important products of copper corrosion in a saline environment. Copper(I) compounds often decompose in the presence of water and additional bands observed in the Raman spectrum of eriochalcite over that of nantokite must be due to the presence of water. In claringbullite ($\text{Cu}_4\text{Cl}[\text{Cl}_{0.29}(\text{OH})_{0.71}](\text{OH})_6$), some water molecules have been replaced by hydroxyl groups in the coordination sphere. Therefore any additional bands observed in the Raman spectrum of claringbullite may be attributed to hydroxyl units. This is important in determining which bands belong to which vibrational unit. The number of formula units in the unit cell and their factor group analysis determines the Raman spectrum of the three minerals, and a detailed analysis of these might yield a convenient method for distinguishing between them in complex mixtures of corrosion products of copper objects.

It is not easy to undertake the infrared spectrum of nantokite, as the mineral reacts quite quickly. The advantage of using Raman spectroscopy is that the freshly cleaved surface can be used as the sample without any further preparation. Raman spectra of the hydroxyl-stretching region of nantokite, eriochalcite and claringbullite are shown in Figure 1. What is important is that for nantokite no hydroxyl stretching bands are observed. This means that the mineral remained unreacted during measurement. The Raman spectrum of the hydroxyl-stretching region of eriochalcite displays an intense band at 3367 cm^{-1} with minor bands at 3462 and 3176 cm^{-1} (Figure 2). The infrared spectrum of eriochalcite shows bands at 3462 , 3352 , 3260 and 3157 cm^{-1} . Multiple bands are observed for eriochalcite as the water molecule hydrogen bonds to the chloride. The band at 3352 cm^{-1} is the most intense and the position of this band corresponds well with the most intense band in the Raman spectrum. A low intensity band is observed in the infrared spectrum at 1620 cm^{-1} and is attributed to the water HOH bending mode. The claringbullite Raman spectrum shows bands at 3458 , 3433 , 3351 , 3331 and 3211 cm^{-1} . Claringbullite contains two independent Cu sites and there are two types of hydroxyl groups in the unit cell. This is evidenced by the two intense bands at 3433 and 3351 cm^{-1} attributed to in-phase and out-of-phase modes. A low intensity band is observed at 1660 cm^{-1} in the Raman spectrum of claringbullite.

The Raman spectra of the 100 to 1000 cm^{-1} region for the three chloride minerals is shown in Figure 3. That of nantokite in this region shows an extremely intense band at 463 cm^{-1} . This band is assigned to the CuO symmetric stretching mode. The second most intense band is observed at 206 cm^{-1} . This band may be assigned to the longitudinal Cu-Cl optic vibration. A band is observed at 155 cm^{-1} and is attributed to the transverse optic vibration. (KAMINOW, I. P. and TURNER, E. H., 1972; MURAHASHI, T. and KODA, T., 1976; PREVOT, B. et al., 1972) Other low intensity bands are observed in the spectrum (Table 1) and may be attributed to combination modes of the LO and TO vibrations and two phonon vibrations.

For eriochalcite, the strongest bands are observed at 405 and 215 cm^{-1} . These bands, as for nantokite are assigned to CuO and CuCl stretching modes. The band at 215 cm^{-1} is ascribed to the longitudinal optic vibration. A low intensity band is

observed at 155 cm^{-1} and is assigned to the TO optic mode. Other bands are observed at 248 and 235 cm^{-1} . Eriochoalcite contains water units. Therefore bands, which are attributable to water, should be found in the spectrum. The hydroxyl-stretching band at 3367 cm^{-1} and the water-bending mode at 1620 cm^{-1} are obvious. What is not so clear is the origin of a low intensity band at around 687 cm^{-1} , present in both the Raman and infrared spectra. The bands in this position are attributed to water librational modes and are shown in Figure 4. Two bands are observed at 690 and 672 cm^{-1} in the Raman spectrum and two bands are observed at 697 and 663 cm^{-1} in the infrared spectrum and are attributed to water librational modes.

The Raman spectrum of claringbullite displays an intense peak at 511 cm^{-1} , which is attributed to the CuO stretching vibration. The band is in a similar position to that of nantokite. The band is considerable broader with a bandwidth of 23.8 cm^{-1} (as FWHM) compared with that for nantokite of 8.4 cm^{-1} . Two bands are observed at 260 and 231 cm^{-1} and may be attributed to the LO modes. A sharp band is observed at 147 cm^{-1} and is assigned to the TO vibration. Three bands are observed in the Raman spectrum of claringbullite at 970 , 906 and 815 cm^{-1} . These three vibrations are attributed to hydroxyl deformation modes.

Conclusions

In this study we have identified vibrations which are attributable to CuO and CuCl stretching modes. Further bands are assigned to the water OH (for eriochoalcite) and hydroxyl OH stretching (for claringbullite). The significance of this work rests with the observation of additional bands for the sequence nantokite, eriochoalcite and claringbullite is followed as a consequence of increased complexity of their structures. Hydroxyl deformation modes are clearly identified.

The spectroscopic measurements have clear implications for studies of the corrosion of copper. (KRATSCHEMER, A. et al., 2002) It is assumed that there is a natural sequence in which corrosion products are formed in the order cuprite-nantokite-eriochoalcite-atacamite-clinoatacamite. (SHARPE, J. L. and WILLIAMS, P. A., 1999) Such a sequence is highly dependent on the conditions under which copper artefacts are transformed by corrosion processes. It is often stated that paratacamite is formed but this is not always correct as paratacamite is strictly a nickelian or zincian, as a result of structural requirements. The mineral most frequently formed is clinoatacamite. The fundamental significance of this research is the application of Raman spectroscopy to the study of corrosion products of copper, bronze and brasses. Typically minerals such as nantokite, eriochoalcite and even more complex minerals such as claringbullite may form. Raman spectroscopy can readily identify these minerals, and the technique is unequivocally established to be the 'first-port-of call' for the unambiguous identification of copper corrosion products when the paramount consideration is the preservation of the sample, intact.

Acknowledgements

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Table 1 Spectroscopic data of the three copper chloride minerals: nantokite (BOUCHARD-ABOUCHACRA, M., 2001), eriochalcite (TANAKA, H. et al., 1987), and claringbullite (TANAKA, H. et al., 1987)

Nantokite CuCl	CuCl (KRAUZMAN, M. et al., 1974)	Eriochalcite CuCl ₂ ·2H ₂ O	CuCl ₂ ·2H ₂ O	CuCl ₂ ·2H ₂ O	Claringbullite Cu ₄ Cl[(OH) _{0.29} (OH) _{0.71}](OH) ₆	Suggested assignment
Raman	Raman	Raman	Raman	Infrared	Raman	
	3462 3367 3317 3176	3462 3352 3260 3157			3458 3433 3351 3331 3211	OH stretching
	1620					HOH bending
					1049	Impurities/ overtones
					970 906 815	Hydroxyl deformation
	690 672	682	694	690 460	579 511 447	CuO stretch
403 393 356	405 390		409	385 298 247	389 356	Two phonon transitions?
262	247				260	LO modes?

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Figure 1 Raman spectra of the hydroxyl-stretching region of (a) nantokite, (b) eriochalcite and (c) claringbullite.

Figure 2 Band component analysis of the hydroxyl stretching region of (a) eriochalcite and (b) claringbullite.

Figure 3 Raman spectra of the region between 100 and 1000 cm^{-1} for (a) nantokite, (b) eriochalcite and (c) claringbullite.

Figure 4 Raman and infrared spectra of the water librational mode of eriochalcite

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Table 1 Spectroscopic data of the three copper chloride minerals: nantokite, eriochalcite, and claringbullite

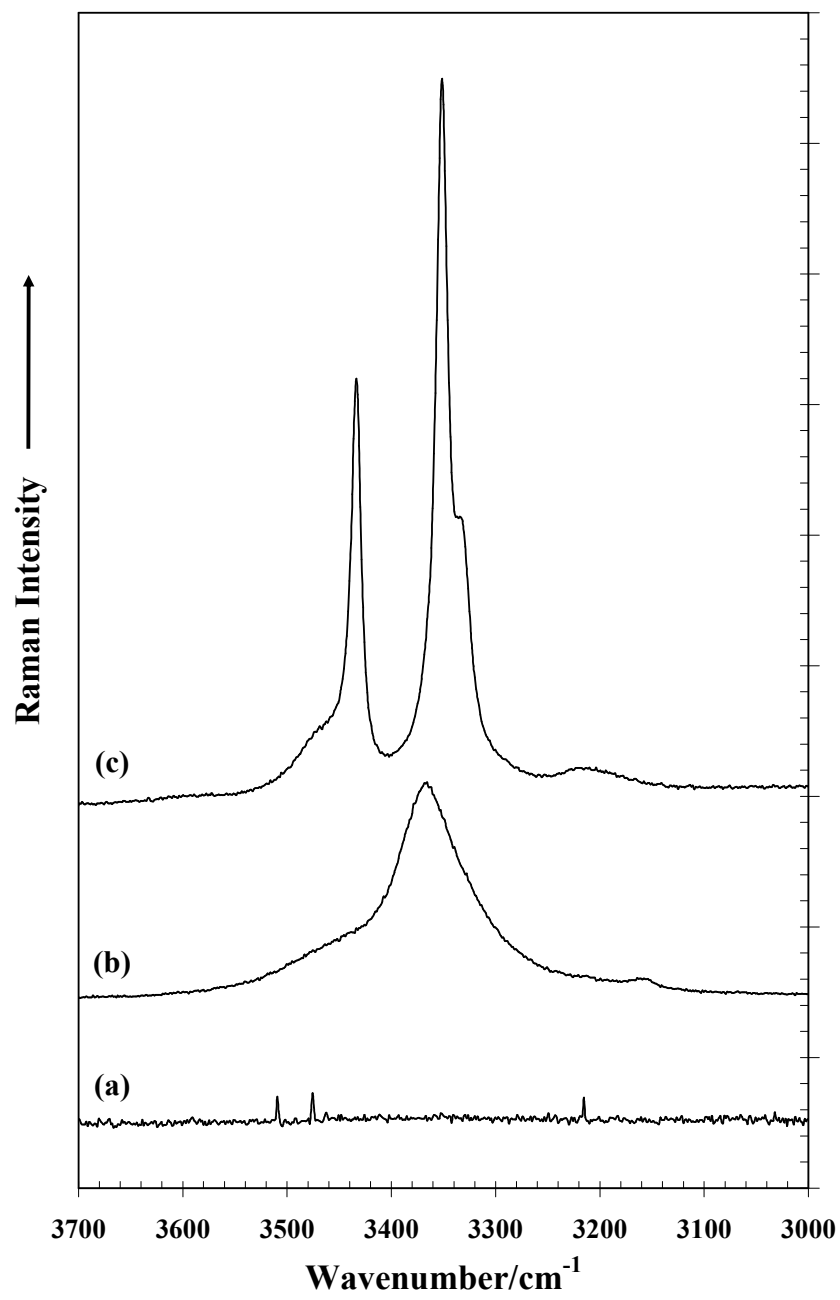


Figure 1

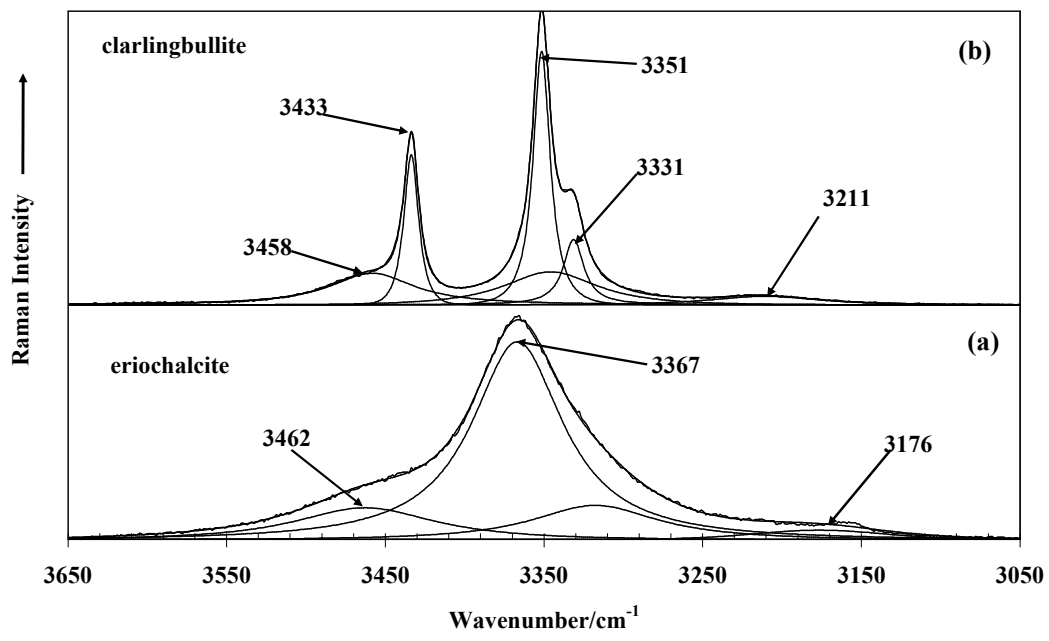


Figure 2

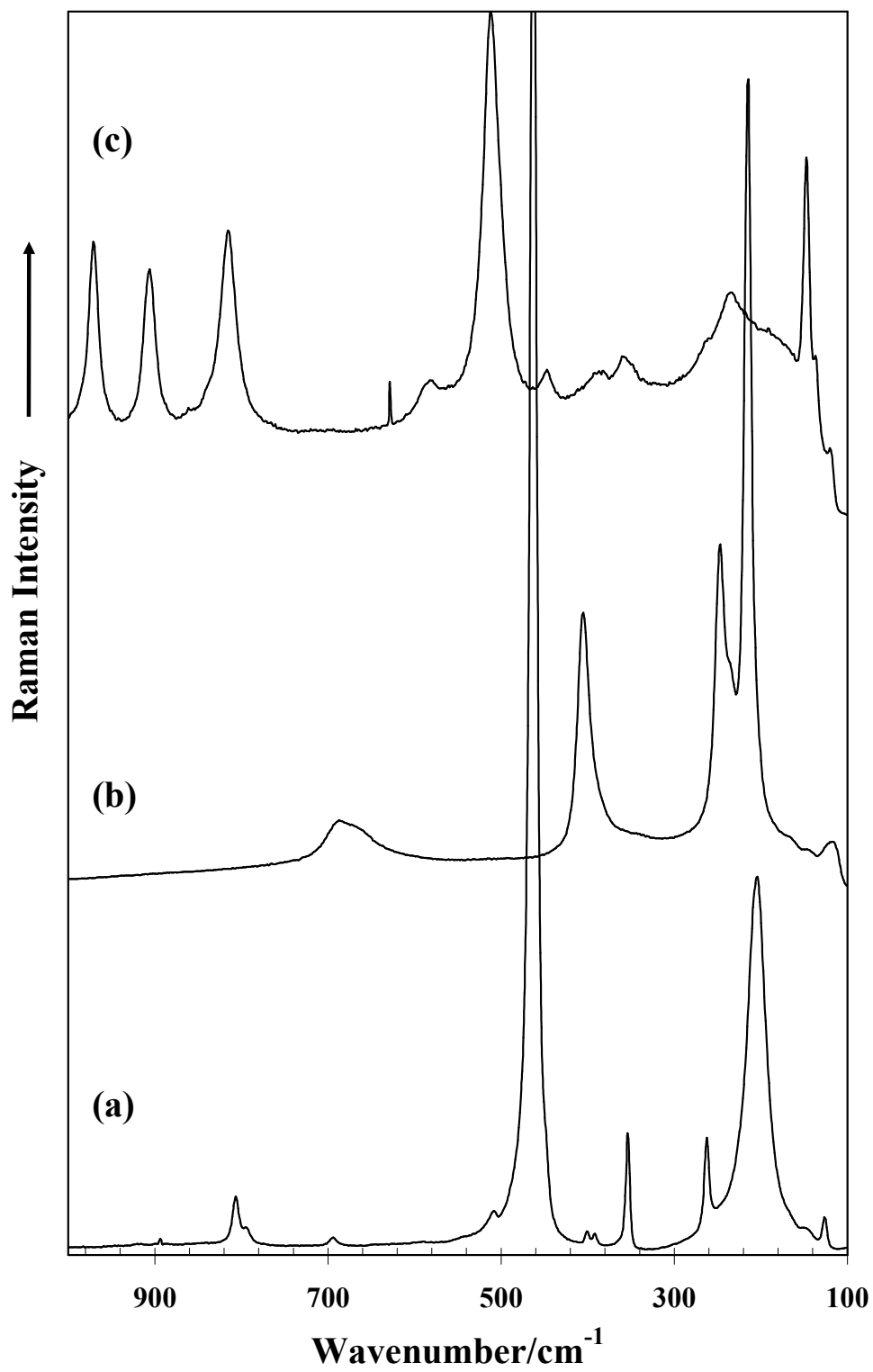


Figure 3

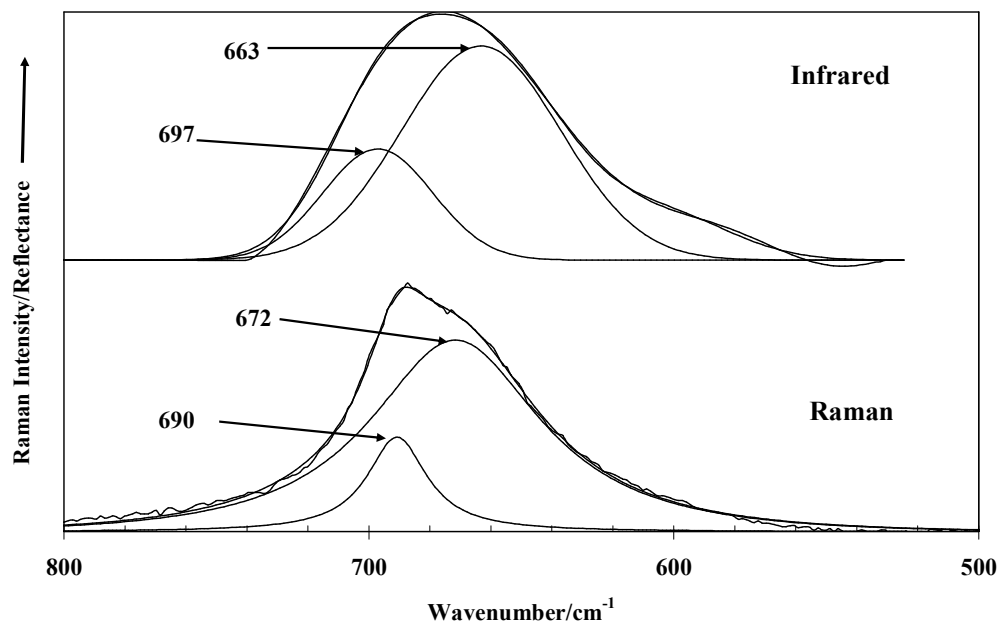


Figure 4