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Raman spectroscopy of some basic chloride containing minerals of lead and copper

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Endnote file: boléite, laurionite, pseudomalachite

ABSTRACT

Raman spectroscopy has been used to characterise several lead and mixed cationic-lead minerals including mendipite, perite, laurionite, diaboléite, boléite, pseudoboléite, chloroxiphite, and cumengéite. Raman spectroscopy enables their vibrational spectra to be compared.   The low wavenumber region is characterised by the bands assigned to cation-chloride stretching and bending modes. Phosgenite is a mixed chloride-carbonate mineral and a comparison is made with the molecular structure of the aforementioned minerals. Each mineral shows different hydroxyl-stretching vibrational patterns, but some similarity exists in the Raman spectra of the hydroxyl deformation modes. Raman spectroscopy lends itself to the study of these types of minerals in complex mineral systems involving secondary mineral formation.

Keywords: boléite, cumengéite, diaboléite, lead, copper, chloride, phosgenite, Raman spectroscopy

INTRODUCTION

The use of these compounds of lead for pharmaceutical and cosmetic purposes in antiquity have been known for some considerable time [1, 2]. Indeed recent chemical analyses have shown that the lead minerals such as crushed ore of galena (PbS) and cerussite ($PbCO_3$) together with laurionite (PbOHCl) and phosgenite ($Pb_2Cl_2CO_3$), were used as cosmetics in Egyptian times [3-5]. The last two minerals are rare in nature and therefore it is inferred that such minerals were synthesised. Ancient literature has provided information on the pharmaceutical preparations of these minerals [5, 6]. Support for this statement comes from recipes of medicinal products to be \"used in ophthalmol.\" reported by Greco-Roman authors such as Dioscorides and Pliny (1st Century B.C.): silver foam (PbO) is crushed and mixed with rock salt and sometimes with natron (Na_2CO_3) [4]. It follows that the Egyptians very early mastered this kind of chemical synthesis and technology, a fact of great importance in the history of science. Fire-based technology had been mastered to manufacture Egyptian Blue pigments during the third millennium B.C. It is now suggested that wet chemistry was already in existence some 4000 years ago.

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A number of these minerals also formed the basis of many paint pigments [7-13]. Many of these pigments were based upon lead dioxide (PbO_2). The Raman spectra of plattnerite [lead(IV) oxide, PbO_2] and of the lead pigments red lead (Pb_3O_4), lead monoxide [PbO, litharge (tetragonal), massicot (orthorhombic)], lead white [basic lead carbonate, $Pb_3(CO_3)_2(OH)_2$] and of their laser-induced degradation products have been measured [12, 13]. The degradation of PbO_2 has been shown to follow the pathway $PbO_2 \rightarrow Pb_3O_4 \rightarrow PbO$ (litharge)$\rightarrow PbO$ (massicot). The shorter the wavelength of the excitation line and the higher its power. The Raman spectrum of PbO_2 showed three bands, at 653, 515 and 424 cm^{-1}, were identified as arising from the B_{2g}, A_{1g} and E_g modes respectively, by analogy with the corresponding modes of isostructural SnO_2 (776, 634 and 475 cm^{-1}). It is noteworthy that minerals such as laurionite and phosgenite, used by the ancient Egyptians, have not been analyzed by Raman spectroscopy. In fact few Raman or infrared spectra of these two minerals have been published.

EXPERIMENTAL

Minerals:

The minerals used in this study have been supplied by the South Australian Museum (SAM). The minerals have been characterized by both X-ray diffraction and by chemical analysis using ICP-AES techniques.

The following samples were used in the study:
(a) Boléite ($KPb_{26}Cu_{24}Ag_9Cl_{62}(OH)_{48}$), SAM G16508[1], from the Amelia mine, Boléo, Baja California, Mexico.
(b) Pseudoboléite ($Pb_5Cu_4Cl_{10}(OH)_8.2H_2O$), SAM G15147, from the Siklverton Barrier Range, New South Wales, Australia.
(c) Perite ($PbBiO_2Cl$), SAM G23884, Homeward Bound Mine, Mannahill, South Australia.
(d) Laurionite (PbCl(OH), SAM G11834, Laurion, Greece
(e) Chloroxiphite ($Pb_3CuCl_2O_2(OH)_2$), SAM G17272, Merehead Quarry, Shepton Mallet, Somerset, UK.
(f) Mendipite ($Pb_3Cl_2O_2$), SAM G17374, Merehead Quarry, Shepton Mallet, Somerset, UK.
(g) Cumengéite ($Pb_{21}Cu_{20}Cl_{42}(OH)_{44}$), SAM G17443, Anticline Deposit, Ashburton Downs, Western Australia.
(h) Diaboléite ($Pb_2CuCl_2(OH)_4$), SAM G14806, Mammath, St Anthony Mine, Tiger, Arizona, USA
(i) Phosgenite ($Pb_2CO_3Cl_2$), SAM G12013, Monteponi, Sardinia, Italy.

Raman microscopy

Crystals of the minerals were placed and oriented 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,

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[1] South Australian Museum registered number

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) and recorded with a resolution of 2 cm^{-1} in the range 100 - 4000 cm^{-1}. Repeated acquisition using the highest magnification was 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. Laser power used was 0.1 mW and typical collection times are ten minutes.

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 range 525 to 4000 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm s^{-1}.

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 specific parameters to be fixed or varied as appropriate. Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands being 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. Such fitting is dependent upon the signal to noise ratio.

RESULTS AND DISCUSSION

Several chloride minerals of the base metals is known from oxidised zones, especially those located in arid areas, or those which are associated with saline ground waters. These minerals often have complex stoichiometry characterised by the presence of more than one anion [14]. These minerals form in ancient slag in seawater as at Laurium, Greece [1, 15-18]. Most of the minerals contain hydroxyl ions. Not only are there mixed-metal species, but minerals with more than one anion as well. Some of the mixed-metal chloride minerals are common. In this work, the mixed chlorides of lead are reported and a selection of minerals is listed in Table 1. The table shows results of Raman spectroscopic analyses. Selection of minerals spans a number of stoichiometries. For example, mendipite is a lead oxychloride and perite is a similar oxychloride containing both lead and bismuth. Phosgenite is a mixed anion example (carbonate-chloride). If hydroxyl replaces the carbonate, the mineral laurionite is obtained. If the Pb is replaced by Cu then the minerals diaboléite, pseudoboléite (a hydrated mineral) and chloroxiphite may be obtained. More complex stoichiometry is exhibited by cumengéite. Recent studies of boléite have shown that there are four cations in the structure [19] although the central K^+ ion maybe in solid solution with Na^+ or H_2O^+ (Williams P.A. unpublished data). These types of minerals lend themselves to Raman spectroscopic analysis; as more complexity is introduced into the structure, this should be reflected in the Raman spectra.

LOW WAVENUMBER REGION

The low wavenumber region of mendipite, perite, phosgenite and laurionite are shown in Figure 1. No sample preparation is involved. Furthermore, Raman spectroscopy readily provides information down to 100 cm^{-1} in contrast to infrared spectroscopy where a 400 to 500 cm^{-1} limit exists depending on the particular infrared spectroscopic technique used. The Raman spectrum of perite (Figure1b) shows two strong bands at 506 and 157 cm^{-1} with other low intensity bands as listed. It is logical to suggest that the strong band at 506 cm^{-1} is attributable to the PbCl and BiCl stretching vibrations and the band at 157 cm^{-1} to the ClPb(Bi)Cl lattice vibration. It is likely that such a band will show longitudinal-transverse optic phenomena. Another band is observed at 364 cm^{-1}, which is assigned to the Pb(Bi)O stretching vibration. Bands at this wavenumber have been observed for other MO bonds. A broad band is observed at 180 cm^{-1} and this may be attributed to the OPbO bending mode. The two latter bands are also observed for mendipite at 161 and 138 cm^{-1}, assigned to the OPbO and ClPbCl bending modes, respectively. For mendipite additional bands are observed at 472, 434, 364, 335, 294 and 272 cm^{-1}. One possible assignment of these bands is that those at 472 and 434 cm^{-1} are due to PbO stretching vibration. No bands are observed in the hydroxyl stretching or water bending regions. A very low intensity band is observed at 972 cm^{-1}, assigned to a sulphate anion, probably due to trace amounts of anglesite (PbSO4) in the mineral sample.

For phosgenite, the spectrum is dominated by two very intense Raman bands at 182 and 152 cm^{-1}, assigned to the A_{1g} and E_g modes of phosgenite, attributed to ClPbCl bending modes [20]. Two low intensity bands are observed at 664 and 649 cm^{-1}. One possibility is that these bands are of A_{1g} symmetry and are attributed to the CuCl stretching modes. It is not clear why the bands are of such low intensity. Very weak bands are also observed at 282 and 252 cm^{-1} in agreement with published data [20]. Since the Raman spectrum of phosgenite will not have any carbonate bands below 400 cm^{-1}, any bands below this may be attributed to PbCl vibrations and translational/rotational modes. This then allows a comparison to be made with the low wavenumber region of the more complex minerals such as boléite, chloroxiphite, cumengéite, diaboléite and pseudoboléite. The Raman spectrum of laurionite is dominated by two intense bands at 328 and 272 cm^{-1}, assigned to the PbCl stretching modes. A band at 131 cm^{-1} is intense and assigned to the ClPbCl bending mode. Other bands are observed at 182 and 176 cm^{-1}. It should be noted that that the low wavenumber region of the Raman spectrum can be readily used to distinguish between the minerals; each has its own characteristic Raman spectrum.

Raman spectra in the low wavenumber region of the other basic lead chloride minerals are shown in Figure 2. The Raman spectrum of diaboléite displays intense bands at 471, 380, 229 and 205 cm^{-1}. The most likely assignment is that the first two bands are due to the PbCl stretching modes and the last two to the ClPbCl bending vibrations. The Raman spectrum of pseudoboléite shows an intense band at 512 cm^{-1} and two intense sharp bands at 179 and 148 cm^{-1}. Both of the latter bands are assigned to the ClPbCl bending modes. The band at 512 cm^{-1} may be attributed to PbCl stretching. Other low intensity bands are observed at 584, 449, 388 and 236 cm^{-1}. The Raman spectrum of chloroxiphite is dominated by a band observed at 139 cm^{-1}. The Raman spectrum of cumengéite, as for chloroxiphite, is dominated by intense bands at 192 and 154 cm^{-1}. These two bands are assigned to ClMCl bending modes where M is Pb or Cu. Other bands are observed at 500, 465, 376, 347, 307, 271 and 154 cm^{-1}. The Raman spectrum of boléite is very similar to that of

cumengéite, which is not unexpected. Two intense bands are observed at 162 and 126 cm^{-1}. These bands are attributed to the ClMCl bending vibrations where M maybe Pb, Cu or Ag; other bands are observed at 458, 363, 302, 257 and 213 cm^{-1}. The bands at around 500 and 450 cm^{-1} for both cumengéite and boléite are attributed to MCl stretching modes.

OH STRETCHING REGION

Mendipite, perite and phosgenite have no hydroxyl units in the structures and no OH stretching bands are observed. Raman spectra of the lead chloride and lead mixed cation minerals are shown in Figure 3. Laurionite shows a single band at 3506 cm^{-1}. The observation of a single Raman band is in agreement with the presence of equivalent OH units in the structure. Laurionite consists of layers of Cl(PbOH)$_2$Cl parallel to its cleavage. In each layer Pb is surrounded by 5Cl at distances of 3.13-3.15 Å., and 3(OH) at 2.64-6 Å [21]. Three bands are observed for diaboléite at 3525, 3478 and 3433 cm^{-1}, being of low intensity. In the structure there are four OH units associated with the Pb cation and four with the Cu cation [22]. Similarly, the Raman spectrum of pseudoboléite displays two intense bands at 3434 and 3551 cm^{-1} with a low intensity band at 3330 cm^{-1} and a broad feature at 3467 cm^{-1}. These Raman features are in agreement with the two distinct positions of the hydroxyl units in the pseudoboléite structure [23]. For chloroxiphite, Raman bands are observed at 3466, 3437, 3400 and 3338 cm^{-1}. The bands are broad although those at 3437 and 3338 cm^{-1} have smaller bandwidths. The width of the bands as compared with those of diaboléite or pseudoboléite is indicative of a range of MOH distances of the OH units in the crystal structure.

The Raman spectrum of cumengéite displays three broad bands at 3588, 3482 and 3413 cm^{-1}, in line with the crystal structure. The cumengéite structure shows a very diverse range of cation coordination, there are 5 distinct Pb sites (with the following coordination polyhedra: octahedron, square antiprism, augmented trigonal prism, distorted biaugmented trigonal prism, and regular biaugmented trigonal prism). There are 2 Cu sites in the structure.

Boléite Raman spectrum displays two bands at 3431 (broad) and 3407 cm^{-1} (sharp) and it is apparent that two types of OH groups are present, one, which is in a fixed distance and a second, which varies in distance from the cation. The Raman spectrum of boléite in some ways is similar to cumengéite. Boléite, KPb$_{26}$Ag$_9$Cu$_{24}$Cl$_{62}$(OH)$_{48}$, is cubic and Pb and Ag atoms form a distorted body-centered array leading to octahedral groupings of these atoms. The Ag atoms and their associated Cl$^-$ ions form Ag$_6$Cl$_8$Cl$_6$ groups similar to those in the metal cluster compounds MoCl$_2$ and WCl$_2$. Pb and Cu ions have distorted square antiprismatic and tetragonal bipyramidal coordination, respectively [19, 24].

Laurionite, diaboléite, pseudoboléite, chloroxiphite, cumengéite and boléite all contain one or more hydroxyl groups and therefore the Raman spectra should also show hydroxyl deformation modes. Figure 4 displays the Raman spectra of the 500 to 1100 cm^{-1} region of these minerals. Laurionite shows two bands at 729 and 594 cm^{-1} with a third band, which may be curve-resolved, at 667 cm^{-1}. The former two bands are assigned to OH deformation modes. In laurionite, each Pb is surrounded by 5 Cl$^-$ ions at distances 3.112-3.344 Å and 3 OH groups at 2.355-2.441 Å. The 4 Cl$^-$ ions

form a rectangle, parallel to *b*, while the 3 OH groups form with the 5th Cl atom a distorted non-planar quadrilateral, 1 diagonal of which is parallel to *b*. The polyhedron is a strongly distorted square antiprism; the Cl atoms are surrounded by 5 Pb^- ions at the vertices of a pyramid, whose base is a rectangle parallel to *b*. Finally, the O atoms are tetrahedrally surrounded by 3 Pb ions and 1 H atom. The 3 Pb atoms form an isosceles triangle with its base also parallel to *b*. The atoms of the asymmetric unit lie on the symmetry plane at *b*/4 and the unit cell may be considered as consisting of 2 layers of atoms, parallel to plane (010) at a separation of *b*/2. Within the layers there is no regular closest packing. The coordination polyhedra around Pb order themselves in zigzag chains parallel to *c* [25].

In the Raman spectrum of diaboléite an intense band is observed at 678 cm^{-1}, which is attributed to the OH deformation. Other low intensity bands are observed at 920, 863 and 783 cm^{-1}, but their assignment is not clear. One possibility is that they are due to overtone or combination bands. The second possibility is that the bands are due to substitution associated with the replacement of the chloride or hydroxyl anions by some other anion. In pseudoboléite three intense Raman bands are observed at 973, 908 and 817 cm^{-1}, paralleling the situation in the hydroxyl-stretching region of pseudoboléite. For chloroxiphite, an intense band is observed at 782 cm^{-1} with two broad bands at 875 and 692 cm^{-1}. Deconvolution of the hydroxyl deformation region appears to mimic that of the hydroxyl-stretching region. For cumengéite, the complexity of the hydroxyl stretching region and the width of the deconvoluted bands is reflected in the hydroxyl deformation region. Bands are observed at 891, 830, 797, 715 and 676 cm^{-1}; those at 984 and 1023 cm^{-1} are thought to be due to minor sulphate substitution. The Raman spectrum of the hydroxyl deformation region of boléite is similar to that of cumengéite with bands observed at 922, 822, 752, 732 and 699 cm^{-1}.

CONCLUSIONS:

Raman spectroscopy conveniently enables the identification of bands attributable to the cation-Cl and cation-OH units. In this systematic Raman spectroscopic study, involving progression through the increased stoichiometric complexity, each mineral has been shown to possess a characteristic Raman spectrum enabling rapid identification.   This is significant with respect to (a) the identification of minerals in the oxidised zones of lead tailing dumps [26-28], (b) corrosion of lead [29-31], (c) restoration of paintings of medieval significance [12, 13, 27, 32], (d) the identification of minerals used in cosmetics in ancient Egypt [4-6, 33], (e) soil remediation studies [34]. Raman spectroscopy is very powerful tool for the analysis of the lead chloride compounds in each of these applications.

ACKNOWLEDGMENTS

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Table 1 Raman spectral analysis of selected chloride minerals of lead (Wavenumber/cm^{-1}).

Mendipite	Perite	Phosgenite	Laurionite	Diaboléite	Pseudoboléite	Chloroxiphite	Cumengéite	Boléite
$Pb_3O_2Cl_2$	$PbBiO_2Cl$	$Pb_2CO_3Cl_2$	$PbOHCl$	$Pb_2CuCl_2(OH)_4$	$Pb_5Cu_4Cl_{10}(OH)_8.2H_2O$	$Pb_3CuCl_2O_2(OH)_2$	$Pb_{21}Cu_{20}Cl_{42}(OH)_{44}$	$KPb_{26}Cu_{24}Ag_9Cl_{62}(OH)_{48}$
			3506	3525 3478 3433	3467 3434 3350 3330	3466 3437 3400 3338	3588 3482 3413	3431 3407
		1672 1518 1384 1327 1304 1293						
		1061 (v_1) 1058 (v_1)						
				920 863	973 908 817	875	1023 984 891	922 822
		833 760 667	729 662 594	783 678		782 692	830 797 715 676	752 732 699
472 433	506 484			471	584 512	482 469	500 465	458

364 337 271	389 367 295 253	282	328 272	380 229	449 388 236	406 350 312 286 266 250	376 347 307 271	363 302 257 213
161 138	180 157	182 176 152	174 142 131	205	179 148 137	226 190 179 166 145 139	243 192 154	162 126

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Figure 2

Figure 3

Figure 4

Raman Intensity

(f)

(e)

(d)

(c)

(b)

(a)

500   600   700   800   900   1000   1100

Wavenumber/cm^{-1}