

Raman spectroscopy of the minerals boléite, cumengéite, diaboléite and phosgenite – implications for the analysis of cosmetics of antiquity

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ABSTRACT

The application of Raman spectroscopy to the study of the mixed cationic Pb-Cu and Pb-Cu-Ag minerals: boléite, cumengéite and diaboléite has enabled their molecular structures to be compared. Each of these three minerals shows different hydroxyl-stretching vibrational patterns, but some similarity exists in the Raman spectra of the hydroxyl-deformation modes. The low-wavenumber region is characterized by the bands assigned to the cation-chloride stretching and bending modes. Phosgenite is also a mixed chloride-carbonate mineral and a comparison is made with the molecular structure of the aforementioned minerals. Raman spectroscopy lends itself to the study of these types of minerals in complex mineral systems of secondary mineral formation.

KEYWORDS: boléite, cumengéite, diaboléite, lead, chloride, phosgenite, Raman spectroscopy.

Introduction

INTEREST in the compounds of Pb for pharmaceutical and cosmetic purposes of antiquity has been known for some considerable time (Lacroix, 1911; Lacroix and de Schulten, 1908). Indeed recent chemical analyses have shown that the Pb minerals such as crushed ore of galena (PbS) and cerussite (PbCO₃) together with laurionite (PbOHCl) and phosgenite (Pb₂Cl₂CO₃) were used as cosmetics in Egyptian times (Martinetto *et al.*, 2001; Tsoucaris *et al.*, 2001; Walter, 1999). It must be noted that the latter two minerals are rare in nature and therefore it is inferred that such minerals were synthesized. Ancient literature has provided information on the pharmaceutical preparations of these minerals (Walter, 1999; Walter *et al.*, 1999). Support for this statement comes from recipes of medicinal products to be “used in ophthalmol.” reported by Greco-Roman

authors such as Dioscorides and Pline (1st Century B.C.): silver foam PbO is crushed and mixed with rock salt and sometimes with natron (Na₂CO₃) (Tsoucaris *et al.*, 2001). It follows that the Egyptians mastered this kind of chemical synthesis and technology very early, a fact of great importance in the history of sciences. Fire-based technology was employed to manufacture Egyptian Blue pigments in the third millennium B.C. It is now suggested that wet chemistry was already in existence some 4000 years ago.

Some of these minerals also formed the basis of many paint pigments (Bersani *et al.*, 2001; Black and Allen, 1999; Brooker *et al.*, 1983; Burgio *et al.*, 2001; Burgio *et al.*, 1999; Burgio *et al.*, 2000). Many of these pigments were based upon lead dioxide (PbO₂). The Raman spectra of plattnerite [lead(IV) oxide, PbO₂] and of the lead pigments red lead (Pb₃O₄), lead monoxide [PbO, litharge (tetragonal) and massicot (orthorhombic)], lead white [basic lead carbonate, 2PbCO₃.Pb(OH)₂] and of their laser-induced degradation products have been measured. The degradation of PbO₂ has

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been shown to follow the pathway $\text{PbO}_2 \rightarrow \text{Pb}_3\text{O}_4 \rightarrow \text{PbO}$ (litharge) $\rightarrow \text{PbO}$ (massicot); the shorter the wavelength of the excitation line, the greater its power. The Raman spectrum of PbO_2 showed three bands, at 653, 515 and 424 cm^{-1} , 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}). What is of particular importance is that the synthetic minerals such as laurionite and phosgenite, which were used by the ancient Egyptians, have not been analysed by Raman spectroscopy. In fact few Raman or infrared (IR) spectra of these two minerals have been forthcoming.

Experimental

Minerals

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

The following samples were used: (a) sample ASM-D49056 boléite from the Amelia Mine, Santa Rosalia, Baja, California, Mexico; (b) sample ASM-D 27575 cumengéite Beleo, Baja California, Mexico; (c) sample ASM D36845 diaboléite from Mannoth mine, Tiger, Arizona, USA; and (d) sample ASM D191881 phosgenite from Consols mine, Broken Hill, South Australia.

Raman microprobe spectroscopy

Crystals of the minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with $10\times$ and $50\times$ 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). 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} . 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.

IR spectroscopy

Infrared (IR) 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} and a mirror velocity of 0.6329 cm/s .

Spectroscopic manipulation such as baseline adjustment, smoothing and normalization were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, New Hampshire, 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 >0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2 >0.995$.

Results and discussion

Phosgenite is an example of a mixed halogen-carbonate species of formula $(\text{Pb}_2\text{CO}_3\text{Cl}_2)$. This mineral is compositionally related to northupite, parisite and bastnäsité but is structurally different, belonging to space group $P4/mbm$ and factor group D_{4h} . The carbonate ion lies on C_{2v} sites and this results in considerable symmetry reduction as may be evidenced by the splitting of the ν_3 and ν_4 bands. The mineral, which is in some ways compositionally related, is diaboléite $(\text{Pb}_2\text{CuCl}_2(\text{OH})_4)$ (Abdul-Samad *et al.*, 1981). In this mineral, stoichiometrically the carbonate has been replaced by hydroxyl units. This is a mixed anionic and a mixed cationic species. The crystal structure of diaboléite, $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$, is tetragonal, $P4mm$, $a = 5.880(1)$, $c = 5.500(2) \text{ \AA}$, $V = 190.1(1) \text{ \AA}^3$, $Z = 1$ (Cooper and Hawthorne, 1995). There is one unique Cu^{2+} position coordinated by four (OH^-) and two Cl^- anions; the Cl^- anions occupy the apical positions, and the Cu octahedron shows the [4+2] distortion typical of Cu^{2+} oxides and oxyalts. There is one unique Pb^{2+} position coordinated by four (OH^-) and four Cl^- anions. All the OH^- units form short (0.246 nm) bonds with Pb^{2+} , and lie to one side of the cation, whereas the Cl^- anions all form long (0.322 and 0.340 nm) bonds with Pb^{2+} , and are on the other side of the cation. Pb^{2+} shows a one-sided coordination typical of stereoactive lone-pair behaviour. There are two unique Cl^-

positions; one is strongly bonded to Cu^{2+} and Pb^{2+} cations, whereas the other is primarily held in place by a network of hydrogen bonds emanating from the (OH^-) groups. The Cu octahedra form corner-sharing chains along the c axis, and these chains are cross-linked by Pb^{2+} cations and by hydrogen bonding.

Bol ite originally written as $\text{Pb}_{26}\text{Ag}_9\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{47}\cdot\text{H}_2\text{O}$ has been found to be of formula $\text{KPb}_{26}\text{Ag}_9\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{48}$ (Cooper and Hawthorne 2000). The crystal structure is distorted cubic (Gossner, 1928; Gossner, 1930; Rouse, 1973). Potassium was detected by electron-microprobe analysis, but the amount determined was only 50% of the amount indicated by site-scattering refinement. However, the refinement results show K to be disordered within a large cage in the structure, and the electron-beam bombardment probably induces rapid migration of K within the structure. The IR spectroscopy showed that there is no H_2O present in the structure (Cooper and Hawthorne, 2000). In some ways cumeng ite is compositionally related to bol ite as it is a mixed cationic-anionic species (Humphreys *et al.*, 1980). The crystal structure of cumeng ite ($\text{Pb}_{21}\text{Cu}_{20}\text{Cl}_{42}(\text{OH})_{40}$) is tetragonal, with unit-cell parameters $a = 15.065$ and $c = 24.436$  , space group $I4/mmm$, $Z = 2$ (Hawthorne and Groat, 1986). The cumeng ite structure shows a very diverse range of cation coordinations. There are five 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 two Cu sites. The coordination polyhedra share elements to form prominent columns or rods of polyhedra parallel to the c axis and centred on the 4-fold axes of the unit cell.

Hydroxyl-stretching bands

The Raman spectra of the four minerals: (a) phosgenite, (b) bol ite, (c) diabol ite and (d) cumeng ite in the 3200 to 3700 cm^{-1} region are shown in Fig. 1. The results of the band component analysis of the separate regions are reported in Table 1. Of course phosgenite contains no water or hydroxyl groups and Raman spectroscopy clearly shows the absence of any hydroxyl-stretching vibrations. X-ray crystallography combined with the application of IR spectroscopy to show the presence/absence of water molecules, indicates that no water molecules are present in the formulae of bol ite, diabol ite and cumeng ite. Only hydroxyl units are present. For bol ite, three Raman bands are observed at 3448, 3408 and 3371 cm^{-1} . The bands are broad with half widths of 71.0, 21.0 and 164 cm^{-1} . One possible interpretation of the first two bands is that they are the antisymmetric and symmetric stretching vibrations of the OH units.

For diabol ite, hydroxyl-stretching bands are observed at 3525, 3465, 3452, 3436 and 3340 cm^{-1} . The band component analysis of the hydroxyl-stretching region for this mineral is shown in Fig. 2a. Infrared analysis was attempted using the diamond ATR cell but was not

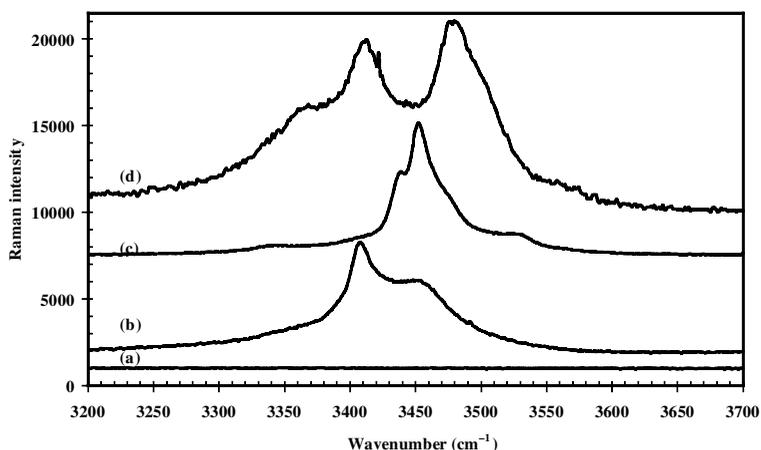


FIG. 1. Raman spectra of the hydroxyl-stretching region of (a) phosgenite, (b) bol ite, (c) diabol ite and (d) cumeng ite.

TABLE 1. Raman spectroscopic results for the minerals: phosgenite, boléite, diaboléite and cumengéite.

Phosgenite					Boléite	Diaboléite	Cumengéite		Suggested assignment
Raman	Raman (Rulmont, 1978)	IR (this work)	IR (Farmer, 1974)	IR (Rulmont, 1978)	Raman	Raman	IR	Raman	
					3448	3525		3588	Hydroxyl stretching
					3408	3465	3466	3482	
					3371	3452		3413	
						3436	3426	3366	
						3410	3358	3340	
1672	1670	1660							Carbonate antisymmetric stretching
1518		1608	1510 (ν_3)	1510					
1384	1417	1378							
1327	1326		1350 (ν_3)	1346					
1304									
1293									
1061 (ν_1)	1062								Carbonate symmetric stretching
1058 (ν_1)									
833	834	838	838 (ν_2)	837	921	978		1023	
760			760 (ν_4)	760	817		846	984	
667	666		653 (ν_4)	650	757	781	794	891	
					731	672	673	830	
					696		632	797	
							594	715	
							563	676	
						538			
								500	
					478	468		465	
					455	437			
					386			376	
				309	361	365		347	
					300	294		307	
282	282				234	227		271	
	252				215			243	
	186						175	192	
182	182						149	154	
176	178				161	130			
	155								
152	152			145	146				
	129			115	128				
	107			91					
				80					
				61					

successful. Spectra could have been obtained by crushing or grinding the samples but this was not possible because the samples are unique and are

on loan. This actually demonstrates the power of Raman spectroscopy, since the spectra can be measured without harming the crystals in any

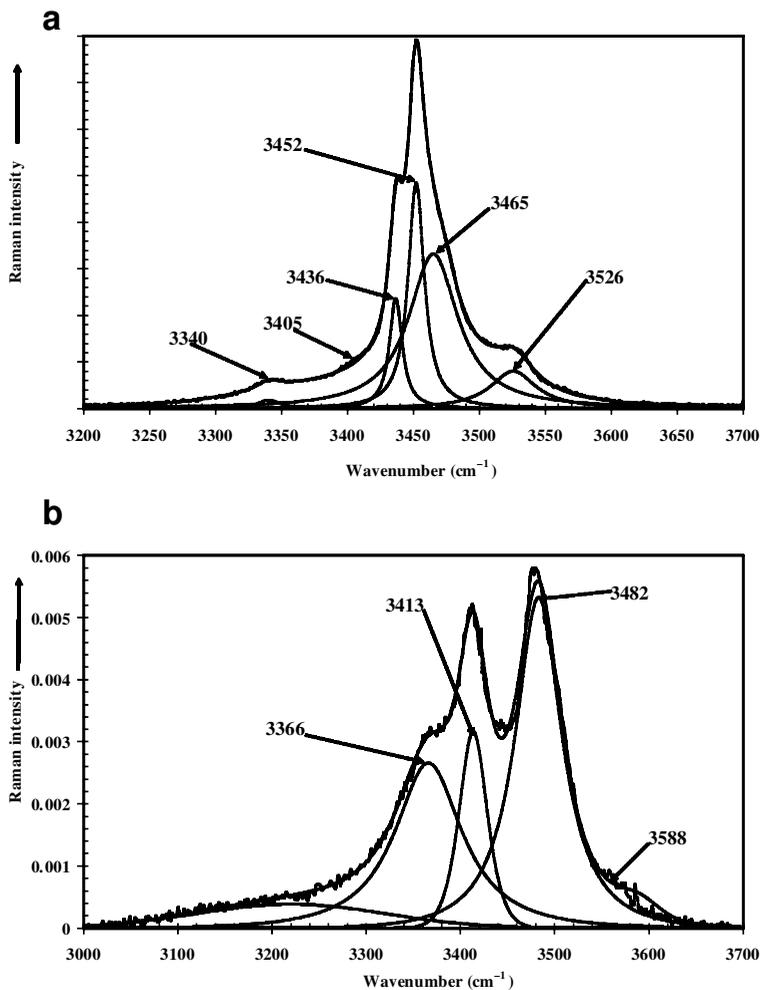


FIG. 2. Band component analysis of the hydroxyl-stretching region of the Raman spectrum of (a) diaboléite and (b) cumengéite.

way. In the crystal of diaboléite there are two cations. The Cu^{2+} is bonded to four OH units in a square plane arrangement. The Pb^{2+} is bonded to four OH units and four Cl^- units. The structure is distorted. It is apparent that the two types of hydroxyl units, depending on whether the OHs are bonded to the Cu^{2+} or the Pb^{2+} , are different. There are apparent in the spectra three sets of bands: (a) 3465 and 3526 cm^{-1} , (b) 3436 and 3452 cm^{-1} and (c) 3340 and 3405 cm^{-1} (very low intensity). The first pair of bands (a) is assigned to the symmetric and antisymmetric stretching vibrations of OH units associated with the Pb cation. The second set of bands is likewise associated with the Cu cation. The question arises

as to the origin of the third set of bands (c). It must be remembered that Raman spectroscopy functions on a picosecond timescale compared with the long-time measurements of X-ray diffraction where a time average structure is determined. It is possible that an interaction occurs between the Cl anion and an adjacent hydroxyl unit and forms a hydrogen bond of the type $\text{Cl}-\text{HO}$ bond. Hence the two bands observed at 3340 and 3405 cm^{-1} are associated with hydroxyl units, which are strongly hydrogen bonded. The Raman spectrum of cumengéite (Fig. 2b) although of low signal to noise ratio, shows three strong bands at 3482, 3413 and 3366 cm^{-1} . Low intensity bands are observed at

3588 and around 3180 cm^{-1} . The structure of the hydroxyls in cumengéite is complex. One possible attribution of the bands is that the 3413 and 3482 cm^{-1} is the symmetric and antisymmetric OH-stretching vibrations. The band at 3366 cm^{-1} may be attributed to the strong OH bond formed through the transient migration of the Cl anion.

Hydroxyl deformation modes of boléite, diaboléite and cumengéite

The Raman spectra of the three lead chloride-hydroxy compounds are shown in Fig. 3. The results of the band component analysis are reported in Table 1. In the low-wavenumber region from 100 to 1000 cm^{-1} , two types of bands will be observed: (a) those ascribed to the hydroxyl deformation modes, and (b) those assigned to the PbCl and CuCl vibrations. The authors have shown in previous publications that the cation-Cl stretching vibrations occur at positions $<550\text{ cm}^{-1}$; therefore the bands in

Fig. 3 must be due to the hydroxyl deformation modes. Sometimes these hydroxyl deformation bands are more definitive than the hydroxyl stretching vibrations because of band overlap of the latter. For boléite, bands attributed to the hydroxyl deformation modes are observed at 921 , 817 , 757 , 731 and 696 cm^{-1} . In the most recent structure of boléite ($\text{KPb}_{26}\text{Ag}_9\text{Cu}_{24}\text{Cl}_{62}(\text{OH})_{48}$) (Cooper and Hawthorne, 2000), there are 48 hydroxyls present. In the hydroxyl-stretching region there were six bands observed. Thus one would expect six hydroxyl deformation modes. We observe five bands, although the band at 817 cm^{-1} is broad and could be resolved into a second component. Thus the analysis of the hydroxyl deformation region is in agreement with that for the hydroxyl-stretching region of boléite.

In contrast, two hydroxyl deformation modes are observed for diaboléite ($\text{Pb}_2\text{CuCl}_2(\text{OH})_4$). For diaboléite, six hydroxyl-stretching vibrations were observed at 3526 , 3465 , 3452 , 3436 , 3405 and 3340 cm^{-1} and two hydroxyl deformation modes at 781 and 672 cm^{-1} are observed. A low-

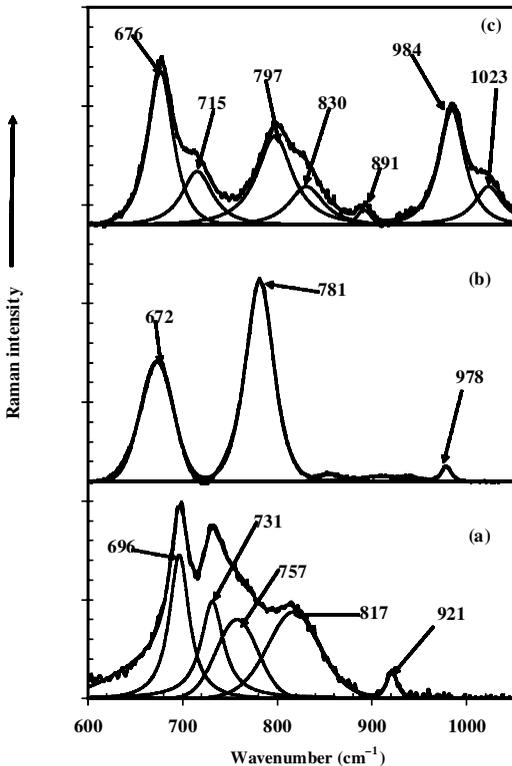


FIG. 3. Raman spectra of the $600\text{--}1000\text{ cm}^{-1}$ region of (a) boléite, (b) diaboléite and (c) cumengéite.

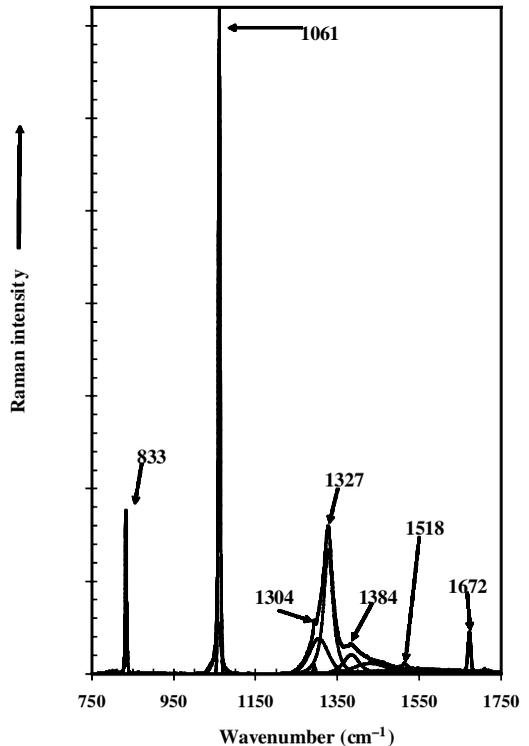


FIG. 4. Raman spectra of the carbonate region of phosgenite.

intensity band at 978 cm^{-1} is also observed. One possibility is that the band may be due to isomorphous substitution by sulphate. If this is the case then the bands at 781 and 672 cm^{-1} are the hydroxyl deformation modes. X-ray diffraction determines a time-averaged structure and low concentrations of sulphate may not be detected by XRD whereas Raman spectroscopy readily detects very small concentrations of sulphate. Such comments are also true for the cumengéite sample. Two bands are observed at 984 and 1023 cm^{-1} , which are assigned to the symmetric and antisymmetric stretching modes of sulphate. There has been some isomorphous replacement of the chloride by sulphate anions in the cumengéite structure. Just as X-ray crystallography suggests, the structure as shown by Raman spectroscopy of cumengéite is complex. This complexity is reflected in the number of hydroxyl deformation modes observed. Bands are observed at 830 , 797 , 715 and 676 cm^{-1} . Since boléite and cumengéite are compositionally related, some similarity between the Raman spectra of these two minerals in the hydroxyl deformation region is observed.

Phosgenite carbonate structure

The chemistry of the mineral phosgenite has been studied for a long time (Ferraris, 1907; Mugge, 1914; Sillen and Pettersson, 1944; Sillen and Pettersson, 1946). The Raman spectrum of phosgenite shows an extremely intense band at 1061 cm^{-1} (Fig. 4). The band is assigned to the carbonate (ν_1) symmetric stretching vibration. A very low-intensity band is also observed at 1058 cm^{-1} . This band may be attributed to the CO stretching vibration of the isotopic CO of carbonate. The bandwidth (as FWHM) of the 1061 cm^{-1} band is 4.8 cm^{-1} . The position of this symmetric stretching vibration is in excellent agreement with that published by Rulmont (Rulmont, 1978). The band is not observed in the IR spectra either in this work or in published results. The second most intense band is that observed at 833 cm^{-1} . This band is assigned to the ν_2 OCO bending mode. A band in this position was reported for the Raman spectrum of synthetic phosgenite (Rulmont, 1978). The bandwidth is 4.0 cm^{-1} , showing an extremely sharp Raman band. Figure 4 also shows bands at 1672 , 1518 , 1384 , 1327 and 1304 cm^{-1} . The positions of these bands are in excellent agreement with published results (Rulmont, 1978). The 1670 cm^{-1} band is also sharp with a bandwidth

of 8.0 cm^{-1} . This band is of A_{1g} symmetry (Rulmont, 1978). The bands at 1384 , 1327 and 1304 cm^{-1} are assigned to the ν_3 modes. The observation of several bands in this position is an indication of the loss of site symmetry of the carbonate anion in the phosgenite structure. The bands at 760 and 666 cm^{-1} are assigned to the ν_4 bending modes. The bands are in good agreement with those published by Farmer (1974).

Low-wavenumber region

The Raman spectrum of phosgenite, boléite, diaboléite and cumengéite in the low-wavenumber region are shown in Fig. 5. For phosgenite, the spectrum is dominated by two very intense Raman bands at 182 and 152 cm^{-1} . These bands have been assigned to the A_{1g} and E_g modes of phosgenite and are attributed to CIPbCl bending modes (Rulmont, 1978). Two low-intensity bands are observed at 664 and

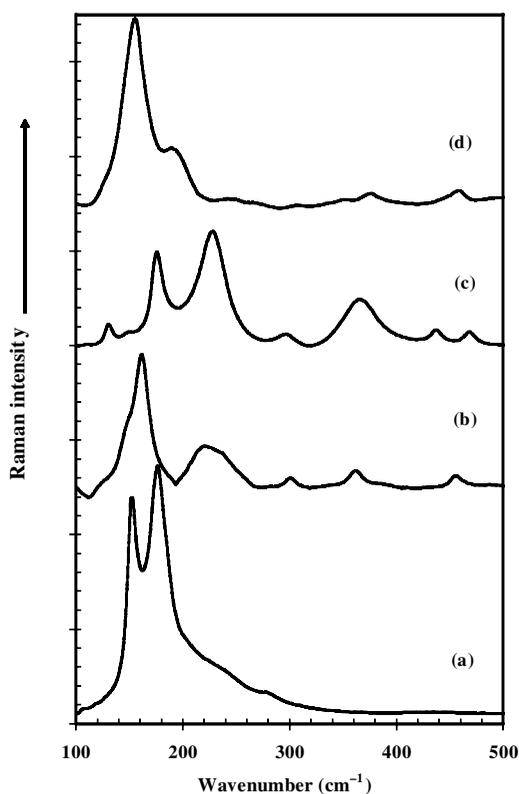


FIG. 5. Raman spectra of the $100\text{--}500\text{ cm}^{-1}$ region of (a) phosgenite, (b) boléite, (c) diaboléite and (d) cumengéite.

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 understood why the bands are of such low intensity. Very low-intensity bands are also observed at 282 and 252 cm^{-1} in agreement with the published data of Rulmont (1978). Since the Raman spectrum of phosgenite will not have any carbonate bands below 400 cm^{-1} , then any bands below this position may be attributed to PbCl vibrational modes. This then allows a comparison to be made with the low-wavenumber region of boléite, diaboléite and cumengéite.

The Raman spectra of the low-wavenumber region can be used to easily distinguish between the four minerals studied. The Raman spectrum of boléite shows Raman bands at 478, 455 and 386, 361, 300, 234, 215, 160 146 and 128 cm^{-1} . The most intense band is that at 160 cm^{-1} . This band is complex and may be deconvoluted into at least two bands at 160 and 146 cm^{-1} . These two bands are assigned to the CIMCl bending modes where $M = \text{Pb, Cu or Ag}$. The two bands at 455 and 361 cm^{-1} may be due to the MCl-stretching vibrations. The bands at 234 and 215 are attributed to hydrogen bonding (OH–O) type vibrations in the structure.

In some respects there is a reasonable comparison between the low-wavenumber spectrum of diaboléite and boléite. Compositionally the two minerals are related. Boléite has Ag in the structure and both minerals are the mixed cationic basic chloride minerals of Pb and Cu. The Raman spectrum of diaboléite shows bands at 468, 437, 365 and 294 cm^{-1} . Further bands below 300 cm^{-1} are observed at 227, 175, 149 and 130 cm^{-1} . The most intense band is observed at 227 cm^{-1} and this band has previously been assigned to the OH–O hydrogen bonding vibrations. The second most intense band is that at 174 cm^{-1} . This band may be compared with the most intense band in the Raman spectrum of boléite at 161 cm^{-1} and is assigned to the CIMCl bending mode where for diaboléite $M = \text{Pb or Cu}$. The ionic radii of Cu^{2+} and Pb^{4+} are 0.072 and 0.084 nm, respectively, whereas the ionic radius of Ag^+ is 0.126 nm. The ionic radii of Cu^{2+} and Pb^{4+} are sufficiently close that the CIMCl band is the same for both minerals. In the case of boléite, two bands are observed at 161 and 46 cm^{-1} . This latter band is probably the ClAgCl bending mode. As for boléite, the bands in the positions at 468, 437 and 365 cm^{-1} may be attributed to the MCl stretching vibrations. In the Raman spectrum of

cumengéite, the most intense Raman band is observed at 154 cm^{-1} with a second intense band at 192 cm^{-1} . Other bands of quite low intensity are observed at 465, 376, 347, 307, 271 and 243 cm^{-1} . The band at 154 cm^{-1} is assigned to the CIMCl bending mode.

Conclusions

Some minerals are of significance in the study of compounds used in pharmaceutical and cosmetic applications in antiquity. Among these minerals is phosgenite. Related to this Pb mineral are the naturally occurring Pb-Cu minerals formed during the complex crystallization of secondary minerals. Included in these minerals are boléite, diaboléite and cumengéite. Raman spectroscopy has been used to determine the molecular structure of the latter three minerals for the first time and a comparison is made to that of phosgenite. The hydroxyl stretching and deformation vibrations of boléite, diaboléite and cumengéite characterize these minerals. Hydroxyl deformation modes are characterized by the mixed cationic species of the mineral. Low-wavenumber regions of the Raman spectra display bands which may be assigned to the cation-chloride stretching and bending vibrations. Raman spectroscopy has been used to determine the molecular structure of these minerals and the three basic mixed cation minerals can be readily distinguished by their Raman spectra, thus making their identification in complex mineral systems easier.

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