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Raman spectroscopic study of azurite and malachite at 298 and 77K

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Azurite $\{Cu^{2+}_3(CO_3)_2(OH)_2\}$ and malachite $\{Cu^{2+}_2(CO_3)(OH)_2\}$ are both monoclinic hydroxy carbonates of copper. The Raman spectra of these two minerals have been collected at both 298 and 77 K together with the single crystal Raman spectra of azurite at 298 K. The spectra of both azurite and malachite contain modes of three separate vibrational groups: OH, CO_3 and Cu-O. Accordingly, for azurite the bands at 3453 and 3427 cm^{-1} have been assigned as the O-H stretching mode with the O-H bending modes found at 1035 and 952 cm^{-1}. Malachite displays two hydroxyl stretching bands at 3474 and 3404 cm^{-1} at 298 K which shift to 3470 and 3400 cm^{-1} at 77 K while O-H out-of-plane bending modes are found at 1045 and 875 cm^{-1}. For the carbonate group, bands are observed at 1090 cm^{-1} (ν_1), 837 and 817 cm^{-1} (ν_2), 1490 and 1415 cm^{-1} (ν_3), and 769 and 747 cm^{-1} (ν_4). The effect of collecting the spectra at 77 K results in considerable band narrowing. The Raman spectra of the single crystals of azurite show the orientation dependence of the vibrational modes. A mechanism for ν_2 splitting is proposed whereby vertical carbonate ions couple to form an in-phase and out of phase bending modes. Combination of these vibrational modes such as $\nu_1 + \nu_3$, $\nu_1 + \nu_3$, $\nu_1 + \nu_4$ and $2\nu_2$ are found at 2530, 2414, 1860, and 1670 cm^{-1}, respectively. IR bands for the Cu-O stretching modes are observed at 495 and 400 cm^{-1}, while Cu-O bending modes occur at 455 and 345 cm^{-1}. Bands at 305 and 240 cm^{-1} are assigned to the O-Cu-OH bending modes. The Raman out-of-plane bending modes are found at 194 and 170 cm^{-1}. For the carbonate group, infrared bands are observed at 1095 cm^{-1} (ν_1), 834 and 816 cm^{-1} (ν_2), 1430 and 1419 cm^{-1} (ν_3) and 764 and 739 cm^{-1} (ν_4). Combination of the CO_3 vibrational modes $\nu_1 + \nu_4$ is observed at 1860 cm^{-1}. IR bands for Cu-O stretching modes are observed at 580, 570 and 505 cm^{-1}.

INTRODUCTION

Azurite $Cu_3(CO_3)_2(OH)_2$, is a relatively rare basic carbonate of copper, which is of importance only because it is a copper ore mineral formed chiefly by the action of carbonated waters on other copper minerals in the upper oxidized zone of ore deposits.[1] Malachite $Cu_2(CO_3)(OH)_2$, is a similar basic carbonate of copper. More common than azurite, it is still only a secondary mineral found in copper deposits. The main interest in these minerals stems from their use in mediaeval art works , thus their identification and analysis via non-destructive means is essential. [2-4] Clark et al. and Edwards et al. used the characteristic Raman spectrum of azurite and malachite to identify pigments in three illuminated mediaeval Latin manuscripts and also in post mediaeval glazed tiles. [2,3]

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Raman and infrared spectroscopy have been used to investigate azurite and malachite before but a detailed single crystal Raman study has not yet been undertaken; yet a full space group analysis has been reported .[5-7] Goldsmith and Ross reported the infrared spectra of azurite and malachite. [5] An infrared stretching vibration of the hydroxyl unit of azurite was observed at 3425 cm^{-1}, whereas two bands were reported for malachite at 3400 and 3320 cm^{-1}. The observation of two bands for malachite suggests coupling of the hydroxyl stretching vibrations. This coupling was not observed for azurite. Azurite and malachite form the basis of pigments in samples of an archaeological or medieval nature. [2,3] In these types of analyses some Raman spectra are reported. However a complete Raman spectroscopic analysis is not required as individual Raman bands are simply used to identify the mineral pigments in the samples. Malachite has a characteristic intense band at ~430 cm^{-1} and azurite an intense band at ~400 cm^{-1}. The deformation modes of azurite were reported at 1035 and 952 cm^{-1} and at 1045 and 875 cm^{-1} for malachite. [5] Thus even though the two carbonate minerals have the same space group, the molecular structure of the minerals is sufficiently different to show infrared bands at slightly different wavenumbers. Differences between the spectra of malachite and azurite may be explained by the molecular structure of azurite being based upon a distorted square planar arrangement compared with a distorted octahedral arrangement about the copper in malachite.

The symmetric stretching bands of carbonate for azurite and malachite were observed at 1090 and 1095 cm^{-1}. Goldsmith and Ross report the infrared bending modes of carbonate at 837 and 817 cm^{-1} for azurite and at 820 and 803 cm^{-1} for malachite. Two v_3 modes were observed at 1490 and 1415 cm^{-1} for azurite and at 1500 and 1400 cm^{-1} for malachite. The observation of these two bands shows a loss of degeneracy. Such a conclusion is also supported by the observation of two v_4 modes at 769 and 747 cm^{-1} for azurite and 710 and 748 cm^{-1} for malachite. The vibrational spectroscopy of these two minerals is complicated by this loss of degeneracy. Schmidt and Lutz report some vibrational spectroscopic data. [8] Two infrared bands at 3415 and 3327 cm^{-1} were observed for malachite. Although the Raman spectra of the mineral brochantite [$Cu_4(OH)_6SO_4$] have been reported, the Raman spectra of malachite and azurite were not. [8] Little attention, however, has been paid to the complete vibrational spectroscopy of these minerals and it is the objective of this work to describe the molecular structure of azurite and malachite through Raman microscopic study of these minerals. The Raman spectra of the two minerals at 298 and 77 K together with the single crystal Raman spectrum of azurite at 298 K are reported.

EXPERIMENTAL

Origin of samples

The azurite sample was collected at Tsumeb mine, Tsumeb, Namibia, South Africa. Malachite was obtained from an Australian source near Broken Hill. A single crystal of approximately 5 mm in the longest dimension was used for orientated single crystal Raman microscopy at room temperature. The phase identity of the crystal was checked with X-ray diffraction, before analysis by Raman microscopy. It is observed

that the phase identity of the samples is correct except for the containment of small amounts of impurities, such as quartz. For Raman spectra at 298 K, the samples were left on the host rock but removed for spectra collected at 77 K. The reason for leaving the mineral on the host rock was to prevent the introduction of impurities.

Raman Microscopy

The samples were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x 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 polarised light at 633 nm and collected at a resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) 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. Raman scattering with 760 nm laser excitation was also used for the low wavenumber part of the spectrum. Although the crystals were still present in the host rocks, alignment of all crystals in a similar orientation has been attempted. However, differences in intensity may be observed due to minor differences in the crystal orientation. The Raman spectra of the oriented single crystals are reported in accordance with the Porto notation.

Spectra at low temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). The azurite sample was removed from the host rock for analysis at 77 K. Samples were placed on a circular glass disc, which fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc.

Infrared spectra were obtained using a Perkin-Elmer FTIR series 2000 spectrometer using the KBr pellet absorption technique. The resolution of the instrument was set at 4 cm^{-1} and 256 scans were collected. For Far-IR spectroscopy, approximately 5 mg of sample were ground for one minute, combined with 250 mg polyethylene and pressed into pellets using 8 tonnes of pressure for five minutes under vacuum. The far-infrared spectra were recorded in triplicate by accumulating 256 scans at 8 cm^{-1} resolution and a mirror velocity of 0.6329 cm s^{-1} between 100 and 580 cm^{-1}, using the Nicolet Nexus 870 Fourier transform far-infrared spectrometer with a DTGS detector and a polyethylene window.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that 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 Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian 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.

Theoretical analysis

The crystal structure of azurite was found to be monoclinic P2$_1$/c. [9] The structure of azurite is based upon the point group C^5_{2h}, with Z = 2, with crystal parameters a = 5.01 Å, b = 5.84 Å, c = 10.34 Å, and β = 92.5º.[4,9] The structure contains two types of Cu atom, both in distorted square planar co-ordination to two hydroxyl groups and two carbonate oxygen atoms. All atoms are on general positions, of site symmetry C$_1$, except for the Cu$_I$ atoms, which are on C$_i$ sites and are co-ordinated to two hydroxyl groups at 1.98 Å and two carbonate oxygen atoms at 1.88 Å, these being in the trans-positions. The Cu$_{II}$ atoms are co-ordinated to hydroxyl groups at 2.04 and 1.99 Å and carbonate oxygen atoms at 1.92 and 2.01 Å, which occupy cis-positions. The carbonate ion itself is undistorted with the OCO angles near 120º. [5]

Malachite crystallises in the monoclinic space group P2$_1$/a with Z = 4. [10] In the structure of malachite, the copper ions Cu^{2+}(1) and Cu^{2+}(2) show the well-known elongated octahedral (4 + 2) coordination. The hydroxide ions are coordinated to three Cu^{2+} ions with two short (~1.91 Å) and one long (~2.36 Å) Cu-O distances.

Tables 1 and 2 display the factor group analyses for carbonate and CuO respectively. Free carbonate ions will usually occupy a D_{3h} point group with Γ$_{vib}$ = A' + A$_2$' + 2E' vibrations under C$_1$ sites reducing to Γ = 6A with consideration of the factor group going to Γ = 6A$_g$ + 6B$_g$ + 6A$_u$ + 6B$_u$. Goldsmith and Ross also noted splitting of the ν$_2$ vibration, which was assigned to the coupling of vibrations with vertical closest neighbours, but this will be discussed later. The skeletal vibrations in azurite can be explained by Γ = 2A$_g$ + 1B$_g$ + 2B$_u$ + 2B$_{2u}$ + 2B$_{3u}$ with C$_s$ site groups allowing Γ = 7A' + 2A'' vibrations. For malachite the vibrations are Γ = 3A$_g$ + 1B$_g$ + 1B$_{2g}$ + B$_{3g}$ + 3B$_u$ + 3B$_{2u}$ + 3B$_{3u}$ as described by Goldsmith and Ross. [5]

RESULTS AND DISCUSSION

The Raman spectra of azurite and malachite at 298 and 77 K are shown in Figure 1. The Raman spectrum of azurite displays an intense sharp band at 3453 cm^{-1}. This band is complex and may be resolved into an additional low intensity component at 3427 cm^{-1}. These bands are assigned to the hydroxyl-stretching modes of the OH unit of azurite. At 77 K these bands are observed at 3446 and 3424 cm^{-1}. The Raman spectrum of malachite shows a broader band in this region with bands observed at 3468 and 3386 cm^{-1} at 298 K. At 77 K the band components are observed at 3349 and 3380 cm^{-1}. Figure 2 displays the infrared spectra collected at 298K of azurite and malachite. The spectra confirm the complex nature of the hydroxyl-stretching region of these two minerals. Hydroxyl-stretching bands in the infrared spectra are observed at 3559, 3424, 3422 and 3271 cm^{-1} for azurite and 3504, 3409 and 3325 cm^{-1} for malachite. The combination of the data from the Raman and infrared spectroscopic analyses proves the non-equivalence of the hydroxyl units in the azurite and malachite structure. Bands are observed in the infrared spectrum of malachite in the 2900 cm^{-1} region. These bands are attributed to a polymer coating on the surface of the detector.

The Raman spectrum of azurite shows a strong band at 1095 cm^{-1}, which does not shift upon cooling to liquid nitrogen temperature (Figure 1). This band is

assigned to the CO symmetric stretching vibration. In the Raman spectrum of malachite two bands were observed at 1101 and 1058 cm^{-1}. Again these bands are assigned to the CO symmetric stretching vibration. This observation leads to the conclusion that at the molecular level there are two distinct carbonate units in the structure. Bands in the infrared spectrum also display complexity in this region with the FTIR spectrum of azurite showing two bands at 1130 and 1069 cm^{-1} and malachite two bands at 1097 and 1048 cm^{-1} (Figure 2). The spectrum of azurite in this part of the spectrum is complex and additional bands are observed. These additional bands are attributed to a loss of degeneracy brought about by local distortions in site symmetry. The azurite Raman spectrum shows a band at 1578 cm^{-1}, which shifts only slightly to 1579 cm^{-1} at 77 K (Figure 1). This band attributed to the carbonate (ν_3) antisymmetric stretching vibration is observed at 1492 cm^{-1} in both the 298 and 77 K malachite Raman spectra. Bands are also observed for azurite at 1483, 1463, 1435, 1415, 1389 and 1383 cm^{-1}. The complexity of this region for azurite results from a loss of degeneracy of the C-O stretching modes. This complexity, however, is not observed for malachite. It is suggested that the malachite has a less distorted structure than that of azurite.

Two bands are observed 834 and 816 cm^{-1} and are attributed to the out of phase and in phase bending modes of the carbonate in azurite. Only a single band at 817 cm^{-1} is observed in this region for malachite. The FTIR spectrum of malachite shows two bands at 879 and 821 cm^{-1}. This FTIR spectral region is more complex for azurite with bands observed at 872, 837, 815 and 796 cm^{-1}. This complexity is again ascribed to the loss of degeneracy. Two bands are observed in the Raman spectra of azurite at 765 and 739 cm^{-1} and are assigned to the ν_4 modes. The equivalent Raman bands for malachite are observed at 765 and 719 cm^{-1}. In the infrared spectra bands are observed at 779, 754 and 701 cm^{-1} for azurite and at 780, 750 and 715 cm^{-1} for malachite.

The Raman spectra of the orientated azurite crystals are shown in Figure 3, with the results of the band component analyses reported in Table 3. Seven Raman bands are observed for the carbonate ion at 1095 (ν_1), 1430(ν_3), 1419(ν_3), 834(ν_2), 816(ν_2), 765(ν_4), and 739 (ν_4) cm^{-1}. The figure and the table clearly show the dependence of the Raman spectrum on the crystal orientation of the azurite. The symmetric ν_1 vibration at 1094 cm^{-1} is most intense in the B(CC)B direction and minimal in the B(AA)B orientation. The ν_2 vibration splitting is also orientation dependent with both the bands at 816 cm^{-1} and 834 cm^{-1} orientation dependent. The 816 cm^{-1} band is most intense in the B(CC)B direction and minimal in the C(AA)C and A(CC)A directions. The implication is that the differential polarisability tensor is aligned close to or along the C(BB)C direction. The intensity of the 834 cm^{-1} band is independent of orientation except for the B(CC)B and B(AA)B directions. This suggests that the direction of the incident radiation is at right angles to the plane of the carbonate. Similar effects are observed for the ν_{3a} and ν_{4a} vibrations. The implication for analyses of these minerals for analytical identification in materials of antiquity is that caution should be exercised in the use of a single band to define the presence or absence of either azurite or malachite. However most samples used for colouring materials of medieval or of an antiquarian nature would be finely ground. Thus the crystal orientations would be randomised.

The structure of azurite is such that carbonate sites are immediately above other carbonate sites. The vibrations of the carbonate are all in plane except the ν_2, bending vibration, which is out of the carbonate plane. This allows for the coupling of this vibration with that of the carbonate ion immediately above. This is the cause of the complexity in this region of the azurite spectrum. This will affect the increase of the energy of the vibration to higher energies. In these experiments the splitting of the ν_2 vibration in to two components at 816 cm^{-1} and 834 cm^{-1} with symmetric and antisymmetric characteristics. However the results of factor group analyses predict ν_1 two Raman and two infrared, ν_2 two Raman and two infrared, ν_3 four Raman and four infrared, and ν_4 four Raman and four infrared bands, described by $6A_g + 6 B_g + 6A_u + 6B_u$. Carbonate combination bands are found at 2530 ($\nu_1 + \nu_3$), 2414 ($\nu_1 + \nu_3$), 1860 ($\nu_1 + \nu_4$), and 1670 ($2\nu_2$) cm^{-1} which are in agreement with the observations of Goldsmith and Ross. [5] Malachite carbonate vibrations are seen to occur at 1096 (ν_1), 817 (ν_2), 1516 (ν_3), 1493 (ν_3), 752 (ν_4), and 710 (ν_4) cm^{-1}, with no combination bands observable.

The space group analysis of the lattice modes of azurite shows nine vibrations for the Cu$_{II}$, as predicted by Goldsmith and Ross. [5] All nine of these vibrations are infrared and Raman active under the point symmetry of C_s, which are 7A' +2A" .
The Cu$_i$ ions occupy a C_i site symmetry which predicts 6 infrared and 3 Raman active modes described by $2A_2 + 2B_{1u} + 2B_{2u} + 3B_{3u}$. These vibrations are found to occur at 495 (A$_g$), 455 (A$_g$), 400 (B$_{3u}$), 345 (B$_{2u}$), 305 (B$_{1g}$), 194 (B$_{1u}$), 170 (B$_{1u}$), and 240 (B$_{1u}$ + B$_{2u}$) cm^{-1}. Results of this study have revealed bands in the Raman spectra at only 400 and 365 cm^{-1}, thus in this study it is hard to confirm the predictions of Goldsmith et al. [5] This study however detected bands in the infrared spectrum at 494, 459, and 397 cm^{-1}. Using Raman scattering with 760 nm laser excitation, bands were detected at 112, 131, 139, 144, 154, 165, 171, 179, 194, 215, 237, 248, 265, 281, 332, 387, 400, and 414 cm^{-1}. Far infrared bands were detected at 172, 179, 188, 199, 209, 218, 225, 235, 251, 256, 306, and 317 cm^{-1}. Table 5 reports a comparison between the low wavenumber region of azurite and malachite as determined by Far-ir and Raman spectroscopy and is compared with published data. [5,8] Goldsmith and Ross reported eight bands for azurite in the 100 to 500 cm^{-1} region and 14 bands for malachite. [7] The far-IR and data reported here are in good agreement. Additional bands as reported by Goldsmith and Ross for azurite are observed. The Raman data for malachite are in good agreement with the infrared data as reported by Goldsmith and Ross and also Schmidt and Lutz. [5,8] Despite this agreement, there are too many observed bands compared with those predicted by factor group analysis. It is proposed that the minerals have a structure with local distortions in site symmetry such that the factor group analysis is not applicable to the structures.

CONCLUSIONS

The Raman spectra of azurite and malachite show complexity. It is difficult to relate the spectra obtained to the factor group analysis. Basically there are too many bands. The factor group analysis of Goldsmith and Ross contains assumptions, which do not allow the prediction of the Raman spectrum of azurite.[5] Azurite and malachite spectra show typical features of the CO_3^{2-}, OH, and Cu-O groups. Factor group analysis has been applied to the minerals. Azurite and malachite can be still

easily distinguished from each other by Raman and infrared spectra due to differences in the crystal space group. Azurite bands are easily assigned to symmetric and antisymmetric modes with the aid of the orientated crystal spectra. Differences in the spectra of malachite and azurite may be explained by the molecular structure of azurite being based upon a distorted square planar arrangement compared with a distorted octahedral arrangement about the copper in malachite. The implication for analyses of these minerals for analytical identification in materials of an antiquity nature is that caution should be exercised in the use of a single band to define the presence or absence of either azurite or malachite. However most samples of antiquity are non-oriented samples.

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Table 1 Factor group analysis of the carbonate ion of azurite

Skeletal	Site	Crystal
D_{3h}	C_1	C_{2h}
A_1		$6A_g$
A_2'	$6A$	$6B_g$
$2E'$		$6A_u$
		$6B_u$

Table 2 Factor group analysis of the CuO vibrations of azurite.

Skeletal	Site	Crystal
	Cu_I	
D_{2h}	C_i	C_{2h}
$2A_g$	$3A_g$	$3A_g$
B_g		$3B_g$
$2B_{1u}$		$6A_u$
$2B_{2u}$	$6A_u$	$6B_u$
$2B_{3u}$		
	Cu_{II}	
C_s	C_1	C_{2h}
$7A'$		
$2A''$	$9A$	$9A$

Skeletal	Site	Crystal
D_{2h}	C_1	C_{2h}
$3A_g$		
B_g		
B_{2g}	15A	15A
B_{3g}		
$3B_{1u}$		
$3B_{2u}$		
$3B_{3u}$		

Table 3 The Factor group analysis of the malachite Cu-O bonds

Table 4 Analysis of the infrared and Raman spectra including single crystal Raman intensities of azurite and malachite

		ν_1	ν_2		ν_3		ν_4	
			Sym	Antisym	B$_2$	A$_1$	B$_2$	A$_1$
Azurite	Raman Band Position:							
	298 K	1095	816	834	1419	1430	765	739
	77 K	1095	815	835	1421	1431	764	739
	IR Band Positions	1099	816	836	1415	1445	762	754
	IR Literature Band Position [2-5]	1088	812	834	1417	1510	768	740
	Raman Band Intensity as a % of Orientated Azurite Crystals							
	C(AA)C	39.4%	-	12.6%	28.9%	1.7%	15.5%	1.8%
		48607		15561	35672	2150	19119	2143
	C(BB)C	35.8%	5.7%	6.3%	15.5%	21.1%	8.9%	6.6%
		]96108	15398	16760	41501	56546	23984	17793
	A(CC)A	53.2%	-	30.7%	4.9%	-	1.1%	10.1%
		27331		15799	2521		545	5201
	A(BB)A	61.6%	1.3%	18.9%	4.4%	-	13.2%	0.6$
		49189	1067	15076	3480		10512	482
	B(CC)B	29.8%	3.2%	5.5%	9.0%	36.7%	10.9%	4.9%
		33022	3526	6121	9951	40586	12064	5443
	B(AA)B	43.5%	2.7%	17.1%	13.3%	7.4%3	11.5%	4.5%
		18339	1138	7191	5629	128	4847	1893

Malachite	Raman Band Positions							
	298 K	1096	816	801	1492 1514	1364 1423	752	717
	77 K	1098	817	807	1493 1514	1365 1423	750	718
	IR Band Positions	1096	821	804	1491 1519	1388 1420	750	712
	IR Literature Band Position [2-5]	1095	820	803	1500	1400	748	710

Table 5 Vibrational data of the low wavenumber region of azurite and malachite

Azurite			Malachite		
Raman	Far IR	Infrared Ref 5	Raman	Infrared Ref 5	Infrared Ref 8
112					
131			130	132	
139			142	142	
144					
154			151	152	
165			166		
171	172	170			
179	179		176	176	
	188				
194	199	194			
	209		205	206	
215	218		217		
	225				
237	235	240			
248	251				

	256				
265			267	278	270
281					
	306	305	294		302
	317		320	325	328
332		345	349	337	
387			389		361
400		400		418	
414			429	428	430
		455	514	522	505
		495	531	528	527
540			563	570	577
			596	580	588

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