

THE RAMAN STUDY OF CERTAIN CARBONATES

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Abstract

Some of the most common carbonates have been investigated by non-contact Raman spectroscopy. The synthetic alkali carbonates K_2CO_3 and Na_2CO_3 have also been studied. The Raman spectrum of aurichalcite is different from that of malachite. This spectrum has a characteristic intense band at 1069 cm^{-1} which is assigned to the ν_1 symmetric stretching mode of the carbonate unit. The two low intensity Raman lines of 1485 and 1507 cm^{-1} may be ascribed to the ν_3 asymmetric stretching modes. To the ν_4 mode (doubly degenerate symmetric bending) are attributed the values of 706 cm^{-1} (ν_{4a}) and 733 cm^{-1} (ν_{4b}). A number of bands with different intensities are observed in the lowest spectral shift (285 , 388 , 430 , 461 and 498 cm^{-1}). These Raman lines are assigned to the CuO and ZnO stretching and bending vibrations. A single band of the OH-stretching modes is observed at 3344 cm^{-1} .

Key words: nonpolarized Raman spectra, carbonates, alkali carbonates, aurichalcite

Introduction

The Raman modes of carbonates, like those of sulfates, are classified into three types (Nakamoto, 1997): (i) vibrations of $(CO_3)^{2-}$ groups (internal modes) (ii) vibrations of hydroxyl molecule (in the case of hydroxyl carbonates $\approx 900\text{ cm}^{-1}$, 1500 - 1600 cm^{-1} and 3400 cm^{-1}), and (iii) vibration modes M-O from the interactions between the cation and O of either $(CO_3)^{2-}$ or OH^- (external or lattice modes).

The carbonate ion $(CO_3)^{2-}$ is a nonlinear four-atomic species and it must have $3(4)-6=6$ normal modes of vibrations (Cotton, 1990). These six normal modes are illustrated in

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figures 1 and 2. The frequency of the fundamental vibration modes of the free carbonat ion are showed in table 1 (Scheetz and White, 1977). The ν_2 mode of $(\text{CO}_3)^{2-}$, which is Raman forbidden in the free ion, remains weak after coupling to the cations in the lattice.

Table 1. The frequency of the fundamental vibrational modes of the $(\text{CO}_3)^{2-}$

Mode	Symmetry	Selection Rules	Frequencies (cm^{-1})
			Scheetz and White (1977)
ν_1 Nondegenerate symmetric stretch	A'_1	Raman	1064
ν_2 Nondegenerate asymmetric (out-of plane) bend	A''_2	IR	-
ν_3 Doubly degenerate asymmetric stretch	E'	IR+Raman	1415
ν_4 Doubly degenerate symmetric (in-plane) bend	E'	IR+Raman	680

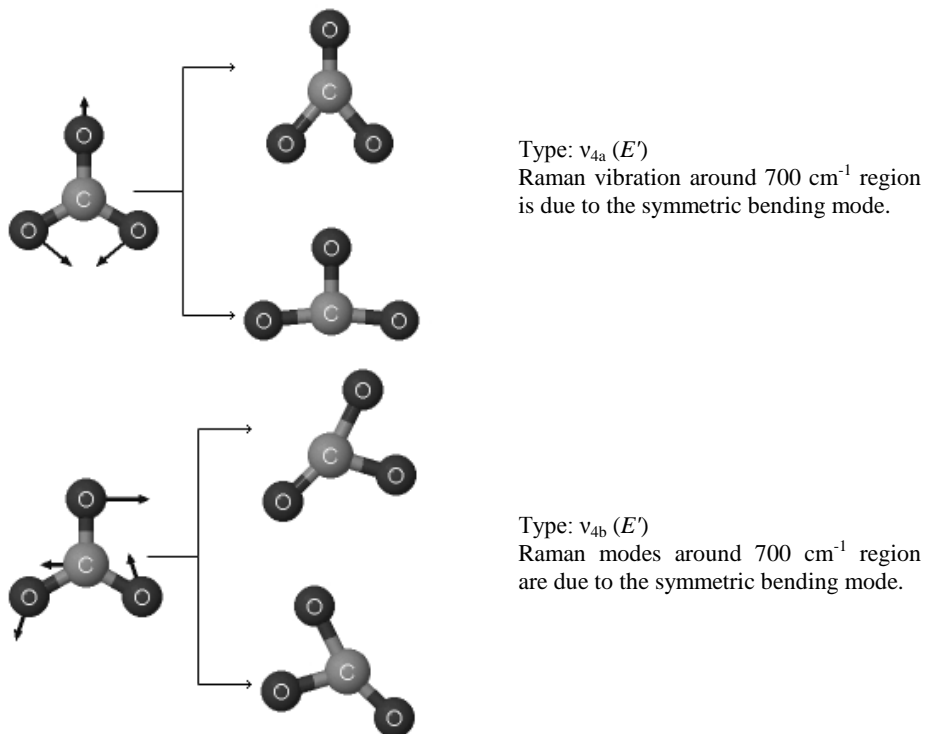


Fig. 1 Illustration for normal modes of vibration; displacement vectors are represented by arrows

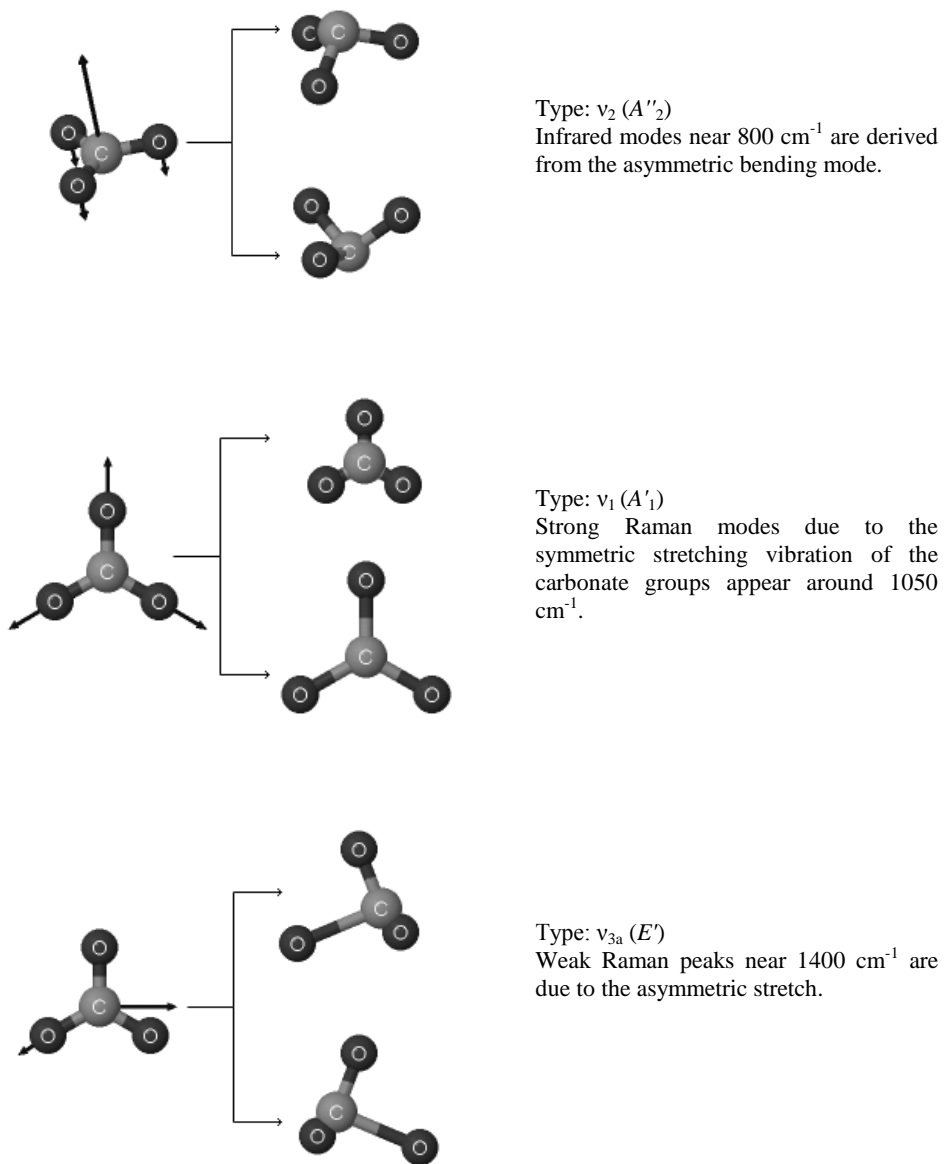


Fig. 2 Illustration for normal modes of vibration; displacement vectors are represented by arrows.

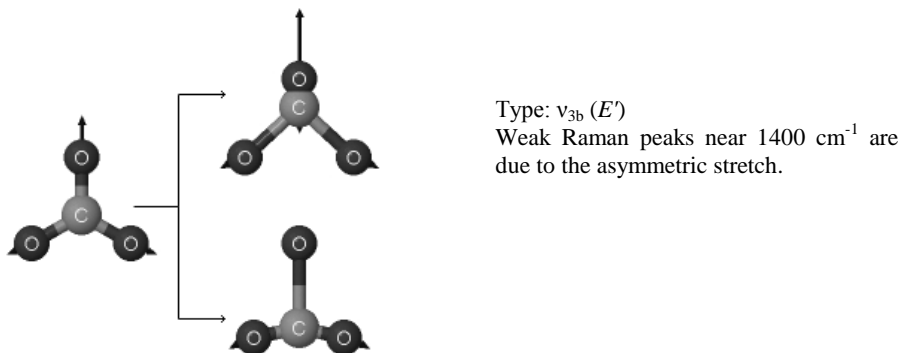


Fig. 2 (continued from the previous page)

Analytical procedure

Raman spectra were obtained at room temperature with a Horiba Jobin-Yvon RPA-HE 532 Raman Spectrograph with multichannel air cooled ($-70\text{ }^{\circ}\text{C}$) CCD detector, using a doubled frequency NdYag laser, $532\text{ nm}/100\text{ mW}$ nominal power. The spectral resolution is $3\text{ cm}^{-1}/\text{pixel}$, and the spectral range between 200 and 3400 cm^{-1} . Raman system includes a “Superhead” fibre optic Raman probe for non contact measurements, with an 50X LWD Olympus visible objective, $\text{NA} = 0.50$ $\text{WD} = 10.6\text{ mm}$.

Data acquisition was performed by 2-20 seconds exposure, 5-30 acquisitions, at laser magnification of 90-100%, to improve the signal-to-noise ratio. Spectra manipulations consists of a basic data treatment, such as baseline adjustment and peak fitting (Lorentz function).

Samples

The samples used in the study are listed in table 2. The first nine samples with their sample number, belong to the collection of “Grigore Cobălcescu” Mineralogy and Petrography Museum of the “Alexandru Ioan Cuza” University of Iassy. The other two samples were synthetic alkaly carbonates.

Results and discussions

A. Anhydrous carbonates

1. Calcite group

Three samples of minerals are used from the calcite group: calcite, siderite and rhodochrosite. The nonpolarized Raman spectra of the calcite, siderite and rhodochrosite are shown in figure 3.

Table 2 Samples used in the study

	Mineral	Sample no.	Location
1.	Calcite	5413	Guanajuato – Mexico
2.	Siderite	5455	Lobenstein – Germany
3.	Rhodochrosite	5438	Kohlenbach – Germany
4.	Aragonite	5421	Spania Dolina – Slovakia
5.	Witherite	5484	Alston – England
6.	Strontianite	5432	Drensteinfurt – Germany
7.	Azurite	5397	Namibia
8.	Malachite	5393	Eisenzeche – Germany
9.	Aurichalcite	5457	Lavrio - Greece
10.	KCO ₃	-	Synthetic
11.	Natrite	-	

The Raman spectra of these minerals are very similar. The intense band (ν_1) of the calcite spectrum corresponds to the symmetric stretching of CO₃ group at 1087 cm⁻¹. The ν_2 (asymmetric bending) vibration mode does not appear. The Raman lines attributed to ν_3 (asymmetric stretching) mode and ν_4 (symmetric bending) mode have 1437 cm⁻¹, respectively 714 cm⁻¹. The Raman spectrum of siderite is characterized by the same Raman band corresponding to the symmetric stretching of CO₃ group as that of the calcite, at 1087 cm⁻¹. The band at 1442 cm⁻¹ corresponds to the ν_3 normal mode and 736 cm⁻¹ to the ν_4 (O-C-O in-plane bending) mode. The Raman spectrum of rhodochrosite consists of a strongest intensity band at 1094 cm⁻¹ assigned to the ν_1 symmetric stretching mode of CO₃ group. The ν_3 normal mode appears at 1439 cm⁻¹ and the ν_4 normal mode at 725 cm⁻¹.

The lower wavenumbers of calcite (285 cm⁻¹), siderite (289 cm⁻¹) and rhodochrosite (292 cm⁻¹) observed in figure 3 arise from the external vibration of the CO₃ groups that involve translatory oscillations of those groups (relative translations between the cation and anionic group). There are no values below 200 cm⁻¹ because the Raman shift is 200-3400 cm⁻¹.

A weak lines observed at 1749, 1729 and 1752 cm⁻¹ may be regarded as the combination bands of $\nu_1 + \nu_4$ modes (Gunasekaran et al., 2006). The spectrum of siderite presents a band at 514 cm⁻¹, which may be assigned to the vibration of a Fe-O bond.

The observed vibrational bands of calcite, siderite and rhodochrosite were compared with their documented values and are listed in table 3. The positions of the observed Raman bands are in agreement with those reported by Gunasekaran et al. (2006) for calcite and Beny (1991) for siderite and rhodochrosite. The minor shift in positions may be due to the effect of natural impurities present in the samples.

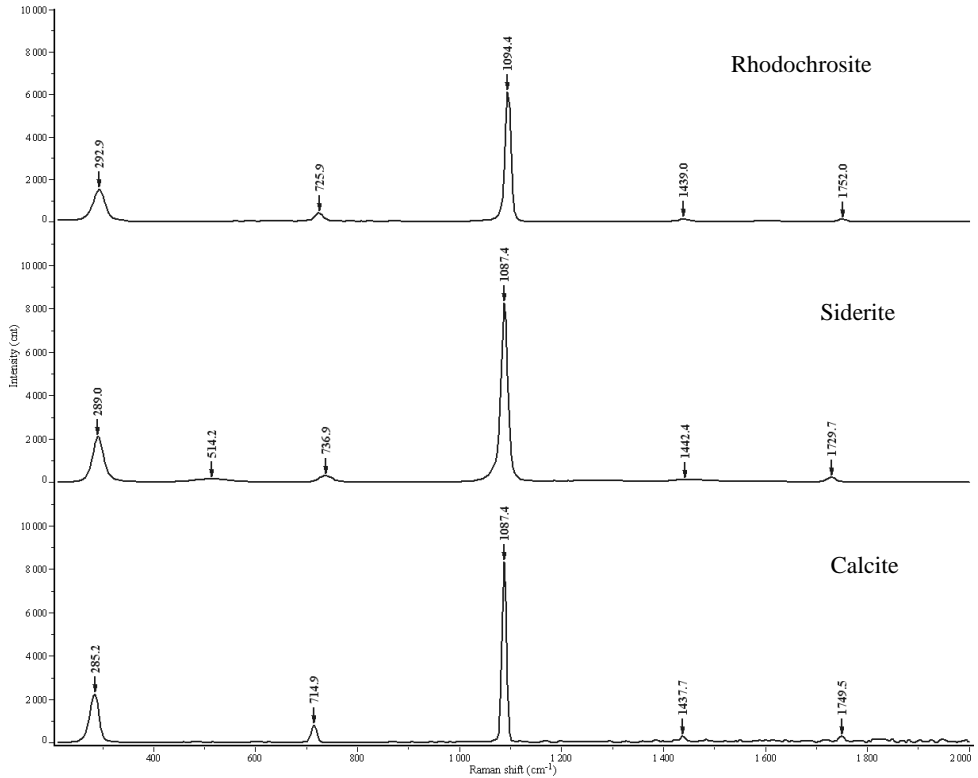


Fig. 3. Raman spectrum of calcite compared with those of siderite and rhodochrosite.

2. Aragonite group

The Raman spectra for the aragonite, witherite and strontianite are shown in figure 4. The spectra of these investigated samples show only five bands out of the 30 predicted Raman-active modes (Krishnamurti, 1960; Urmos et al., 1991). These spectra are governed by the very strong Raman line attributed to the ν_1 symmetric stretching mode of the carbonate group. The wavenumbers of this Raman band are 1083, 1069 and 1059 cm^{-1} (tab. 4). They are similar to those reported by Urmos et al. (1991), Krishnamurti (1960) and Beny (1989).

Table 3. Raman bands in calcite, siderite and rhodochrosite (cm⁻¹)

Calcite		Siderite		Rhodochrosite		Free CO ₃ ²⁻	Assignment
This study	Gunasekaran et al., 2006	This study	Beny (1991)	This study	Beny (1991)		
	89						R*(CO ₃)
	162		190		184		T(Ca, CO ₃)
285	288	289	294	293	289		T(Ca, CO ₃)
		514	506				T(Fe, CO ₃)
715	716	737	731 742	726	718	680	v ₄ -Symmetric bending mode
						879	v ₂ -Asymmetric bending mode
1087	1092	1087	1087	1094	1064 1085	1063	v ₁ -Symmetric stretching mode
1437	1437	1442		1439	1414	1415	v ₃ -Asymmetric stretching mode
1749	1754	1729	1726 1733	1752	1725		v ₁ + v ₄

R* - rotational

The Raman lines attributed to the v₃ asymmetric stretching mode can be observed at 1422 and 1511 cm⁻¹ for witherite, 1445 and 1543 cm⁻¹ for strontianite, respectively 1461 and 1573 cm⁻¹ for aragonite. The appearance of two lines corresponding to v₃ is in accordance with the splitting of v₃ predicted by theory. The Raman lines at 693, 700 and 701 cm⁻¹ were assigned to the v₄ normal mode. The v₂ vibration mode are not visible in our spectra. The Raman bands due to the external vibration mode for aragonite, strontianite and witherite have the frequencies 250, 242 and 227 cm⁻¹. The frequencies of all Raman bands observed in this study can be correlated with the atomic masses of the cations.

3. Alkali carbonates

The Raman spectrum of K₂CO₃ (fig. 5) shows a couple of bands at 1026 and 1063 cm⁻¹ that may be attributed to the v₁ symmetric stretching mode (tab. 5). The two bands may be explained by the presence of the molecules belonging to two structures, C_{2v} bidentate form and D_{3h}, in agreement with the theoretical values calculated by Koura et al. (1996). The v₂ vibration mode is not Raman active. The bands at 1374 cm⁻¹ and 1426 cm⁻¹, can be assigned to v_{3a} respectively v_{3b}. To the v₄ mode (doubly degenerate symmetric bending) are attributed the values of 677 cm⁻¹ (v_{4a}) and 702 cm⁻¹ (v_{4b}). The spectrum also presents three bands at 237 cm⁻¹, 287 cm⁻¹ and 484 cm⁻¹, which may be assigned to the external vibration modes between the cation and anionic group (T(K,CO₃)).

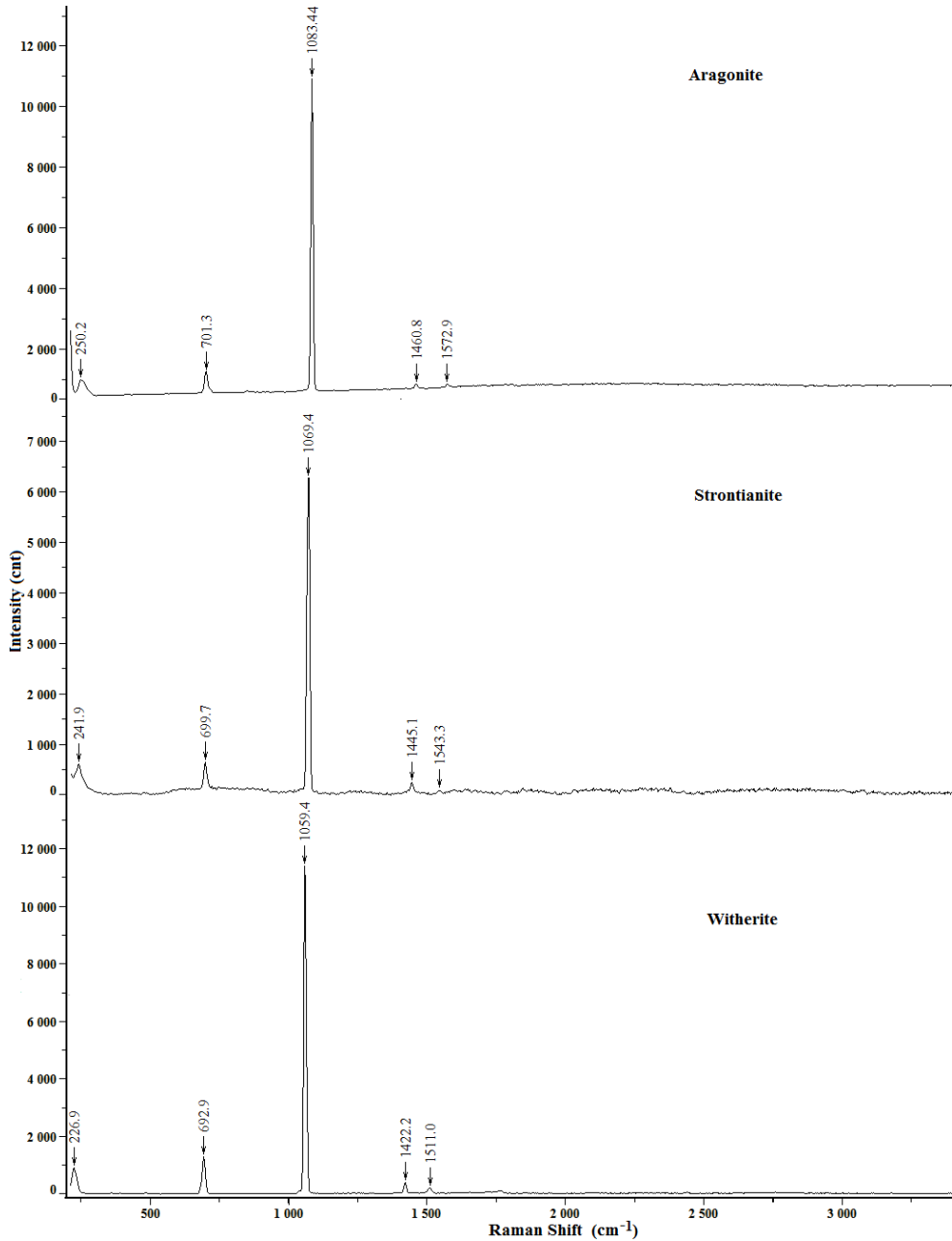


Fig. 4 Raman spectra of aragonite, strontianite and witherite.

Table 4. Raman bands in aragonite, strontianite and witherite (cm⁻¹)

Aragonite			Strontianite		Witherite			Assignment
This study	Urmos (1991)	Krishnamurti (1960)	This study	Krishnamurti (1960)	This study	Krishnamurti (1960)	Beny (1989)	
250	284	285	242	246	227	227	224	T(M,CO ₃)
701	701 705 -	702 707 716	700 - -	701 711 -	693 - -	691 699 -	690 696 -	v ₄
NO	853	854	NO	855	NO	852	-	v ₂
1083	1085	1086	1069	1074	1059	1061	1035 1059	v ₁
- 1461 1573	- 1462 1547	- 1415 1463	- 1445 1543	1408 1438 1447	- 1422 1511	1394 1409 1421	- 1419 1505	v ₃
NO		2165			NO	2116*		2v ₁

NO = not observed; NA = not assigned

Table 5. Frequencies of the Raman lines of the alkali carbonates

K ₂ CO ₃			Na ₂ CO ₃			Assignment
This study	Koura et al. (1996)		This study	Beny (1988)	Burgio and Clark (2001)	
	Calculated	Measured				
237, 288, 484	76, 85, 122, 252, 278, 291	126, 141 192	290	111, 131 149, 171 189	NI*	T (K, CO ₃) T (Na, CO ₃)
677	688	692	702	701	702	v _{4a} (E') Symmetric bending mode
702	706	697				v _{4b} (E') Symmetric bending mode
1026 1063	1025	1043 1064	1080	1069 1079	1071 1081	v ₁ (A ₁ ') Symmetric stretching mode
1374	1385	1405	1429	1421 1431	NI*	v _{3a} (E') Asymmetric stretching mode
1426	1557					v _{3b} (E') Asymmetric stretching mode

NI – Raman bands which appear in the Figure 48 (Burgio and Clark, 2001) but without determined frequencies

For Na₂CO₃, the most intense Raman band, corresponding to the v₁ symmetric stretching vibration of the carbonate group, is at 1080 cm⁻¹. The 1429 cm⁻¹ peak

corresponds to the ν_3 normal mode and line of 702 cm^{-1} is attributed to the ν_4 symmetric bending mode. The Raman spectrum of Na_2CO_3 shows only one line of lattice mode, at 290 cm^{-1} . The wavenumbers of Raman lines for two alkali carbonates are presented in table 5.

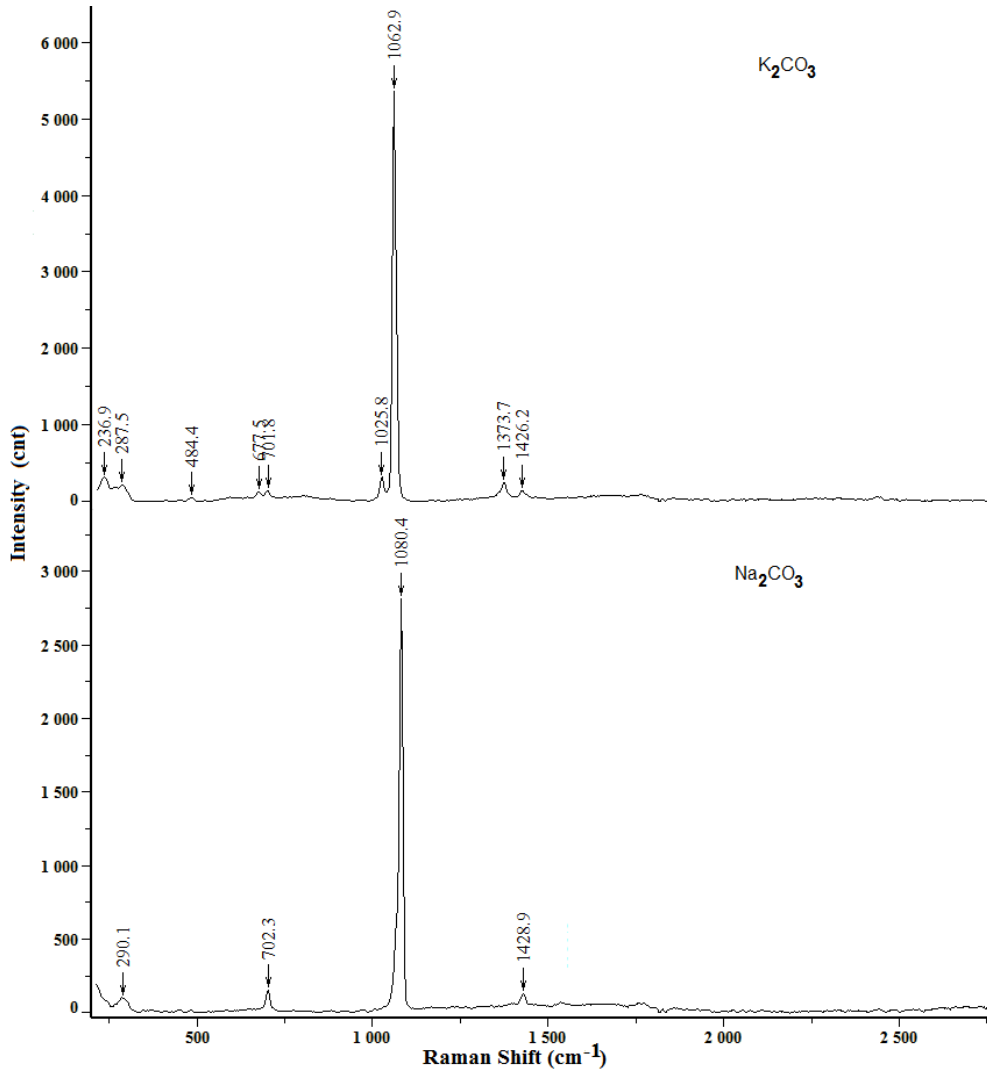


Fig. 5 Raman spectra of alkali carbonates (synth.)

B. Carbonates with hydroxyl

1. Azurite

The spectrum of azurite is shown in figure 6. The wavenumbers of the detected bands are reported in table 6. This azurite spectrum is characterized by several lines that cover the spectral range of 200-1600 cm^{-1} . The bands observed up to 600 cm^{-1} are assigned to the translations of (Cu, CO_3) and those observed up to 1600 cm^{-1} are assigned to CO_3 complex (Frost et al., 2002). The Raman spectrum of our azurite does not show the O-H stretching band at about 3400 cm^{-1} .

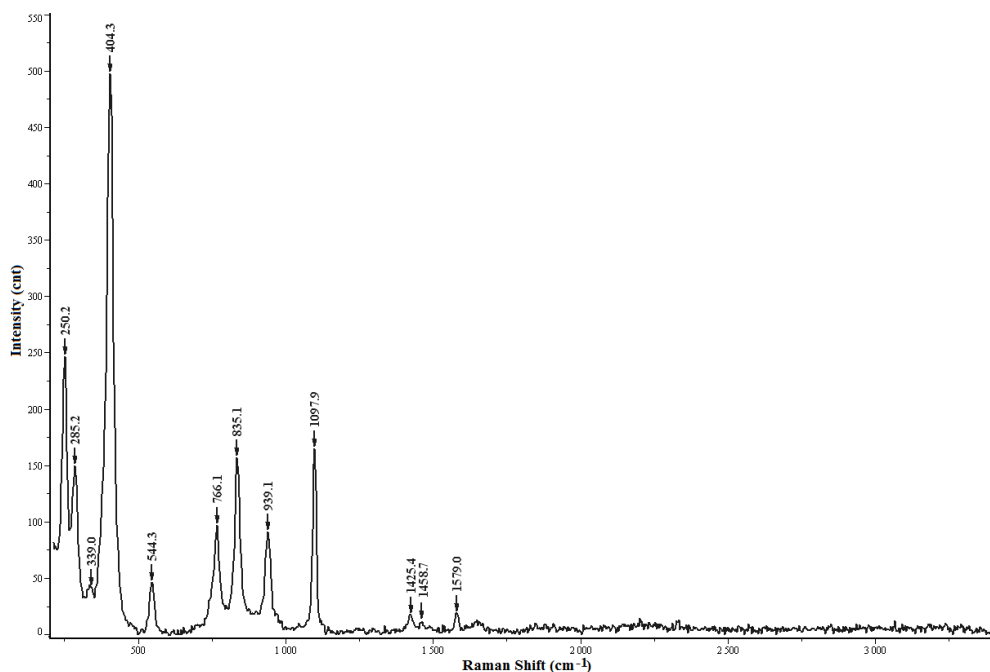


Fig. 6. Raman spectrum of azurite in the 200-3400 cm^{-1} region

Azurite has a characteristic intense band at 404 cm^{-1} . The ν_1 symmetric stretching band of the carbonate ion is observed at 1098 cm^{-1} . The bands attributed to the carbonate (ν_3) asymmetric stretching vibration appear at 1425 cm^{-1} and 1459 cm^{-1} . One band is observed in the Raman spectrum of azurite at 766 cm^{-1} and is assigned to the ν_4 mode. The band of 835 cm^{-1} was assigned to the ν_2 asymmetric bending vibration. A number of bands with different intensities are observed in the lowest spectral shift of the Raman spectrum of

azurite (250, 285, 339, 404 and 544 cm^{-1}). These Raman lines are assigned to the lattice modes. The O-H out-of-plane bending mode of azurite was reported at 939 cm^{-1} . We have not found any information available for Raman line of 1579 cm^{-1} . It is probably due to the O-H bending mode, in agreement with Nakamoto (1997).

Table 6. Raman bands of azurite (cm^{-1})

This study	Azurite		Assignment
	Frost et al., 2002	Mattei et al., 2008	
250, 285, 339, 404, 544	112, 131, 139, 144, 154, 165, 171, 179, 194, 215, 237, 248, 265, 281, 332, 387, 400, 414, 540	157, 174, 182, 240, 250, 267, 282, 332, 387, 402, 542	T(Cu, CO ₃)
766	739 764	744 768	ν_4 -Symmetric CO ₃ bending mode
835	815 835	840	ν_2 -Asymmetric CO ₃ bending mode
939	952	937	O-H out-of-plane bending mode
1097	1095	1099	ν_1 -Symmetric CO ₃ stretching mode
1425 1459	1421 1431	1422 1433 1462	ν_3 -Asymmetric CO ₃ stretching mode
1579		1582	O-H bending mode
NO	3424 3446	3431	O-H stretching mode

NO = not observed

2. Malachite

The Raman spectrum of malachite is shown in figure 7. Malachite has two characteristic very strong bands at 435 and 1495 cm^{-1} .

As in the case of azurite, the Raman bands at the lowest region of the spectrum of malachite (fig. 7) can be attributed to the lattice modes (tab. 7). In this region the spectrum shows an intense band at 435 cm^{-1} , and the others at: 215, 270, 354, 537 and 597 cm^{-1} .

The characteristic bands for the CO₃ group are observed at: 1059 and 1098 cm^{-1} for the ν_1 symmetric stretching modes (of two different CO₃ groups – doubly degenerate mode); 820 cm^{-1} attributed to the ν_2 asymmetric bending mode (Frost et al., 2002); 1368, 1462 and 1495 cm^{-1} assigned to the ν_3 asymmetric stretching modes; 722 and 755 cm^{-1} for ν_4 symmetric bending (doubly degenerate mode). For the hydroxyl-stretching region, the

spectrum shows bands at 3310 and 3382 cm^{-1} . The vibration mode of the hydroxyl group (O-H bending mode) appears at 1639 cm^{-1} .

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 of the copper in malachite (Frost et al., 2002).

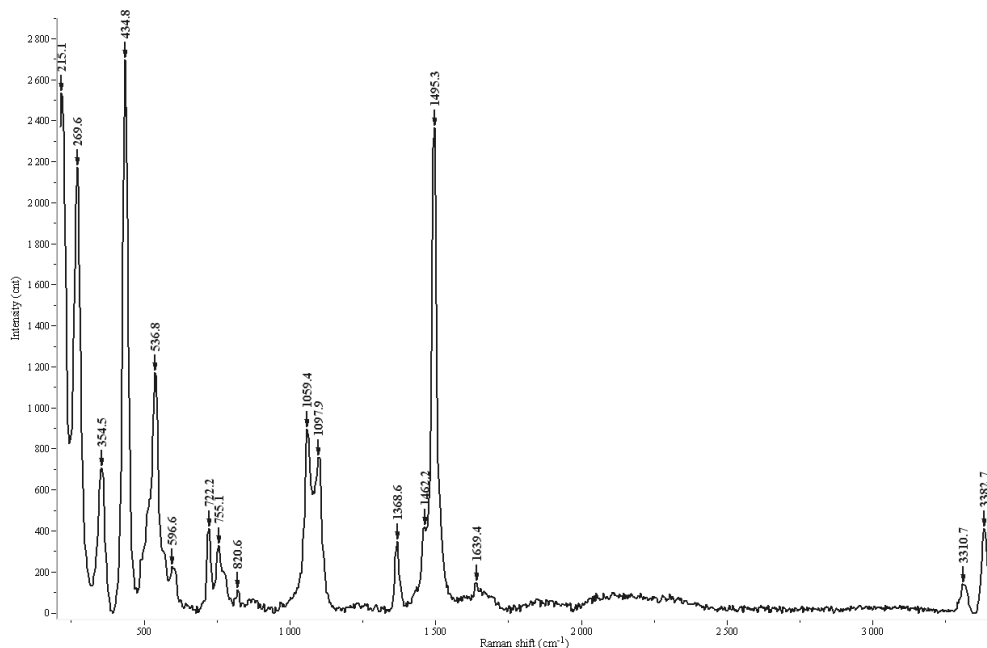


Fig. 7. Raman spectrum of malachite in the 200-3400 cm^{-1} region.

3. Aurichalcite

The Raman spectrum of aurichalcite is different from those of malachite and azurite. This spectrum has a characteristic intense band at 1069 cm^{-1} which is assigned to the ν_1 symmetric stretching mode of the carbonate unit (fig. 8, tab. 8).

The two low intensity Raman lines of 1485 and 1507 cm^{-1} may be ascribed to the ν_3 asymmetric stretching modes. To the ν_4 mode (doubly degenerate symmetric bending) are attributed the values of 706 cm^{-1} (ν_{4a}) and 733 cm^{-1} (ν_{4b}). A number of bands with different intensities are observed in the lowest spectral shift of the aurichalcite Raman spectrum (285, 388, 430, 461 and 498 cm^{-1}). These Raman lines are assigned to the CuO and ZnO

stretching and bending vibrations (Frost et al., 2007). A single band of the OH-stretching modes is observed at 3344 cm^{-1} .

Table 7. Raman bands in malachite (cm^{-1})

This study	Malachite		Assignment
	Frost et al. (2002)	Mattei et al. (2008)	
215, 269, 354, 434, 536, 596	130, 142, 151, 166, 176, 205, 217, 267, 294, 320, 249, 389, 429, 514, 531, 563, 596	157, 171, 182, 204, 224, 272, 352, 435, 513, 537, 601	T(Cu, CO ₃)
722 755	718 750	723 753	v ₄ -Symmetric CO ₃ bending mode
820	807 817		v ₂ -Asymmetric CO ₃ bending mode
1059 1097	1098	1058 1101	v ₁ -Symmetric CO ₃ stretching mode
1368 1462 1495	1365 1423 1493 1514	1370 1463 1497	v ₃ -Asymmetric CO ₃ stretching mode
1639			O-H bending mode
3310 3382	3349 3380	3380	O-H stretching mode

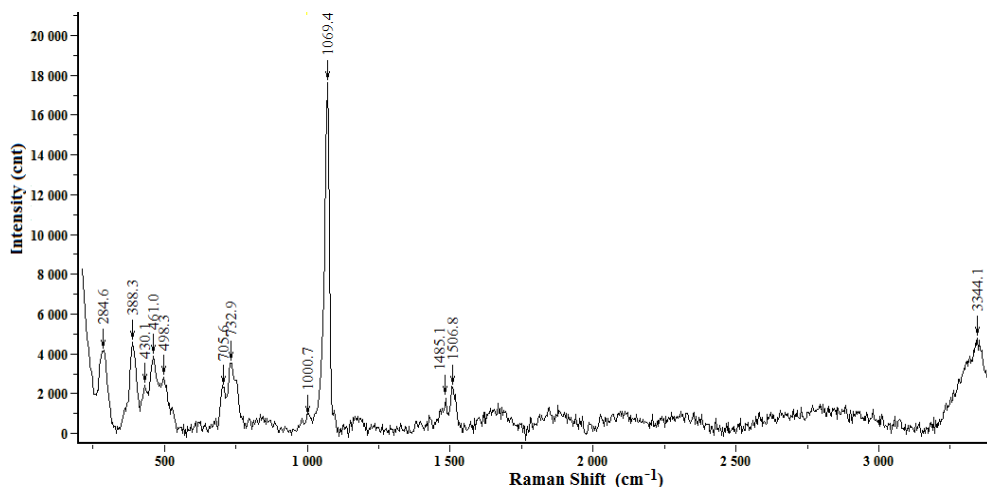


Fig. 8. Raman spectrum of aurichalcite

Table 8. Raman bands in aurichalcite (cm^{-1})

This study	Frost et al. (2007)	Assignment
285, 388, 430, 461, 498	278-283, 388-392, 428-432, 460-463, 498-499	T(Cu, CO_3) and T(Zn, CO_3)
706 733 -	708-711 733-737 748-753	ν_4 -Symmetric CO_3 bending mode
-	849-860	ν_2 -Asymmetric CO_3 bending mode
1000 1069 -	1020 1060-1065 1071-1072	ν_1 -Symmetric CO_3 stretching mode
1485 1507	1485 1506-1511	ν_3 -Asymmetric CO_3 stretching mode
3344	3338-3355	O-H stretching mode

Conclusions

In all spectra the three fundamental vibration modes of $(\text{CO}_3)^{2-}$ were observed, with variations in band positions and splitting, caused by the influences of the different structures and cations.

The measured Raman bands of analyzed carbonates are similar to those reported in literature (ν_1 between 1000-1100 cm^{-1} , ν_2 -800-900 cm^{-1} , ν_3 - 1400-1500 cm^{-1} , ν_4 - 690-790 cm^{-1}). The slight differences between some Raman spectra were probably caused by either the instruments and techniques or the composition of the minerals.

Although the ν_2 vibration mode is not normally active in Raman, it makes an exception in the case of the azurite and malachite samples.

The frequencies of all Raman bands of the orthorhombic carbonates (the aragonite group) can be correlated with the atomic masses of the cations. In the case of trigonal carbonates (the calcite group), the frequencies of the vibrational modes of $(\text{CO}_3)^{2-}$ and the atomic masses of cations cannot be correlated.

The Raman spectrum of malachite and aurichalcite are different although the two minerals have similar structures.

Acknowledgments

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