

THE RAMAN STUDY ON CERTAIN SULFATES

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Abstract

Some of the most common sulfates have been investigated by non-contact Raman spectrography. For barite and anhydrite group the vibrational mode ν_1 decreases as the atomic mass increases. The Raman spectrum of chalcocyanite shows two strong bands at 1013 cm^{-1} and 1045 cm^{-1} interpreted as ν_1 modes. The bands at 423 cm^{-1} , 448 cm^{-1} , 480 cm^{-1} and 514 cm^{-1} have been assigned to the ν_2 sulfate mode, the bands at 1101 cm^{-1} and 1205 cm^{-1} to the ν_3 vibrational modes and the bands at 622 cm^{-1} and 670 cm^{-1} to the ν_4 mode of SO_4 . The bands at 250 cm^{-1} , 269 cm^{-1} and 347 cm^{-1} have been interpreted as vibrations of Cu-O bonds. Szmikite shows intense vibrations at 1021 cm^{-1} interpreted as ν_1 mode of SO_4 . The ν_2 and ν_3 modes the bands are at 425 cm^{-1} and 493 cm^{-1} respectively 1089 cm^{-1} and 1189 cm^{-1} . The bands at 623 cm^{-1} and 654 cm^{-1} were assigned to the ν_4 mode. The translational mode T(H_2O , Mn) was determined at 263 cm^{-1} .

Key words: Raman spectra, sulfates, chalcocyanite, szmikite

Introduction

Raman modes of sulfates are classified into three types: (i) vibrations of SO_4^{2-} groups, (ii) vibrations of H_2O , and (iii) vibration modes M-O from the interactions between the cation and O of either SO_4^{2-} or H_2O (Nakamoto, 2009).

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The sulfate group has four fundamental vibrational modes of SO_4^{2-} , and in aqueous solution it is characterized by the following Raman bands (Omori, 1968): (i) nondegenerate ν_1 symmetric stretching at 981 cm^{-1} , (ii) doubly degenerate ν_2 symmetric bending at 451 cm^{-1} , (iii) triply degenerate ν_3 asymmetric stretching at 1104 cm^{-1} , and (iiii) triply degenerate ν_4 asymmetric bending at 613 cm^{-1} . Reduction in symmetry in the crystal structure of sulfates will cause the splitting of these vibrational modes. Every atom of the SO_4 molecule in solution vibrates freely, but in the crystal, the atom vibrates under additional influences from the cations, and this cause the variation in the wave number of the absorption band (Omori, 1968).

Vibration modes of M-O bonds appear in Raman spectra in the region below 400 cm^{-1} . The cause for these bands is the vibrations of the bonds between the metal cation and the oxygen of the sulfate ion, or in case of hydrated sulfates, the bond between metal cation and the oxygen of water molecule.

Vibration modes of the water molecule are: ν_1 symmetric stretching; ν_3 asymmetric stretching and ν_2 bending. In the liquid state, rotations tend to be restricted by hydrogen bonds, giving the ν_L librations (Lemus, 2004). The ν_1 and ν_3 modes are present in spectra in $3300 - 3500\text{ cm}^{-1}$ region, and are due to the symmetric and asymmetric stretching of the O-H bond. The ν_2 mode in the Raman spectra are located from ~ 1400 to $\sim 1700\text{ cm}^{-1}$. The Raman intensities of the ν_L bands are, in general, in metal sulfate hydrates, more weak and difficult to detect in comparison with those in IR spectra, due to a possible obscuration from the more intense SO_4 modes (Chio et al., 2007).

Micro-Raman studies for most of the sulfate group minerals have been published in the past two decades (Beny, 1991; Chio et al., 2007; Dimova et al., 2006; Klopogge et al., 2001, 2002; Lasnier, 1991; Liu et al., 2009; White, 2008). However, the Raman spectra for chalcocyanite and szmikite are less known. The vibrational modes of these minerals have been investigated by using a non-contact (non-polarised laser beam) Raman spectrometer. Some of the most studied sulfates have been investigated to test the reliability of the data.

Analytical procedure

Raman spectra were obtained at room temperature with a Raman Spectrograph Horiba Jobin-Yvon RPA-HE 532 with multichannel air cooled (-70°C) CCD detector, using a wavenumber doubled Nd-Yag laser, 532 nm and nominal power 100 mW . The spectral resolution was 3 cm^{-1} , 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 $50\times$ LWD visible objective Olympus, $\text{NA} = 0.50$ $\text{WD} = 10.6\text{ mm}$.

Data acquisition was performed by 2 - 6 seconds exposure, 20 - 200 acquisitions, at laser magnification 90 - 100%, to improve the signal-to-noise ratio. Spectra manipulations consists in a basic data treatment, such as baseline adjustment and peak fitting (Lorentz function).

Samples

The samples used in the study are listed in Table 1. The first eight samples with their sample number, are monocrystals which belong to „Grigore Cobălcescu” Mineralogy and Petrography Museum of the „Al. I. Cuza” University of Iassy. The other six samples are synthetic crystalline powders.

Table 1. Samples used in the study

	Mineral	Sample no.	Location
1	Barite	5502	Duften – England
2	Celestine	5515	Gloucestershire – England
3	Anglesite	5558	Monte Poni, Sardinia – Italy
4	Anhydrite	5536	Bleiberg, Carinthia – Austria
5	Linarite	5523	Cumberland – England
6	Gypsum	5492	Cavnic – România
7	Bieberite	5535	Bieber, Hesse – Germany
8	Syngenite	5559	Kalusch – Ukraine
9	Arcanite	-	Synthetic
10	Chalcocyanite	-	
11	Melanterite	-	
12	Epsomite	-	
13	Goslarite	-	
14	Szmikite	-	

Results and discussion

A. Anhydrous Sulfates

1. Barite group

Three minerals from barite group were used for this study: barite, celestine and anglesite. The Raman spectrum of barite (Fig. 1) consists in an intense ν_1 band which corresponds to the symmetric stretching of SO_4 tetrahedra at 989 cm^{-1} . The other characteristic bands, ν_2 , ν_3 and ν_4 , were found at: $\nu_2 - 461 \text{ cm}^{-1}$; $\nu_3 - 1085 \text{ cm}^{-1}$, 1143 cm^{-1} and 1167 cm^{-1} ; $\nu_4 - 619 \text{ cm}^{-1}$ and 648 cm^{-1} (Table 2). For celestine, Raman spectrum (Fig. 1) is also dominated by an intense ν_1 band (1003 cm^{-1}) and the other characteristic vibrational modes of SO_4 group: $\nu_2 - 461 \text{ cm}^{-1}$; $\nu_3 - 1111 \text{ cm}^{-1}$, and 1160 cm^{-1} ; $\nu_4 - 622 \text{ cm}^{-1}$ and 641 cm^{-1} . These values are similar to those reported in the literature (Table 2).

The anglesite spectrum (Fig. 1) is characterised by the same ν_1 band at 978 cm^{-1} . The rest of the vibrational modes have been found at frequencies of 450 cm^{-1} and 553 cm^{-1} for ν_2 ; 1058 cm^{-1} and 1157 cm^{-1} for ν_3 ; and for ν_4 – 611 cm^{-1} and 646 cm^{-1} (Table 2).

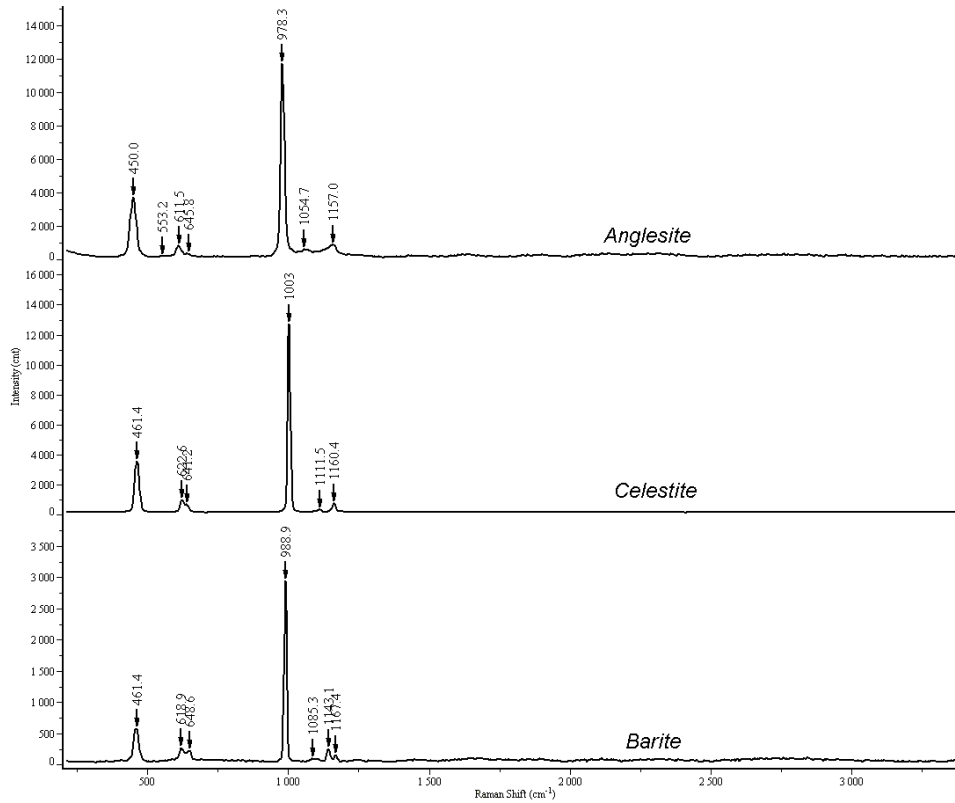


Fig. 1. Raman spectra of barite, celestine and anglesite

The peak corresponding to the symmetric stretching mode (ν_1) of the S–O bond in the sulfates appears to be the strongest in the Raman scattering intensity. The wavenumber of a Raman shift is determined by the bond strength and the atomic masses (Fadini and Schnepel, 1989). Therefore, the ν_1 wavenumber is a function of S–O stretching force constant in sulfates and increases with an increase in the force constant. The force constants of SO_4 tetrahedra were calculated from the bond lengths and the infrared absorption frequencies by Miyake et al. (1978). The stretching force constants are: for barite $K = 6,27\text{ md/\AA}$; for celestine $K = 6,34\text{ md/\AA}$; and for anglesite $K = 5,98$

md/Å. Therefore, this systematic wavenumber shift is largely due to the increase of mean force constants because of substitution of larger cations in the M sites (Lee et al., 2005). Also, the wavenumber decreases with an increase of the atomic mass of the cations. An example for ν_1 mode is presented in Figure 2, where the atomic masses are: Sr = 87.62 u; Ba = 137.32 u; Pb = 207.2 u.

Table 2. Raman bands for barite, celestine and anglesite (cm^{-1})

Vibration modes	Barite		Celestine		Anglesite	
	This study	Dimova et al., 2006	This study	Kloprogge et al., 2001	This study	Beny, 1991
ν_2		453		453	450	437
	461	462	461	460		449
					553	
ν_4	619	618	622	620	611	617
	648	647	641	640	646	640
				659		643
ν_1	989	988			978	977
			1003	1003		
ν_3	1085			1096	1058	1051
	1143	1140	1111	1112		1140
	1167	1167	1160	1162	1157	1155

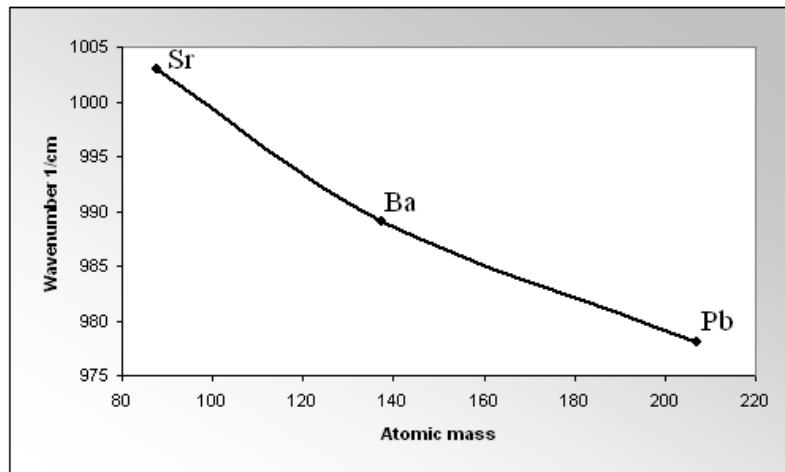


Fig. 2. Wavenumbers of the ν_1 vibrational Raman mode vs. atomic mass of the cations for barite group

2. Anhydrite, arcanite, chalcocyanite, szmikite and syngenite

Raman spectrum for anhydrite (Fig. 3) shows the ν_1 mode at 1017 cm^{-1} . The ν_2 and ν_3 modes of sulfate tetrahedra split in two bands: one at 419 cm^{-1} and 503 cm^{-1} and the other one at 1129 cm^{-1} and 1160 cm^{-1} . The values attributed to ν_4 vibration mode are at 630 cm^{-1} and 678 cm^{-1} . An additional band has been observed at 235 cm^{-1} , which was attributed to an external mode of vibration in anhydrite crystal.

The ν_4 asymmetric bending mode at $609 - 612\text{ cm}^{-1}$ reported by Bhagavantam (1938) and Liu et al. (2009), has a very weak intensity and it is integrated in 630 cm^{-1} band. Bhagavantam also reported a frequency at 1110 cm^{-1} . In our spectrum, this line is overlapped by the 1129 cm^{-1} band. The spectrum of anhydrite presents a weak band at 235 cm^{-1} , which may be assigned to the vibrational mode of Ca-O bonding (Table 3). The band at 3395 cm^{-1} , was assigned to the water stretching mode. Most probably the water was absorbed on the mineral surface from the air.

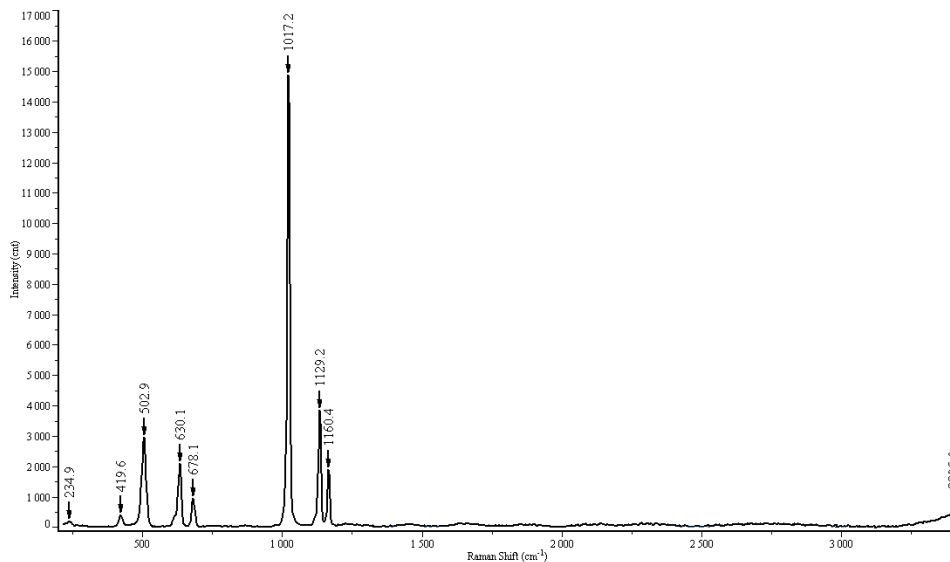
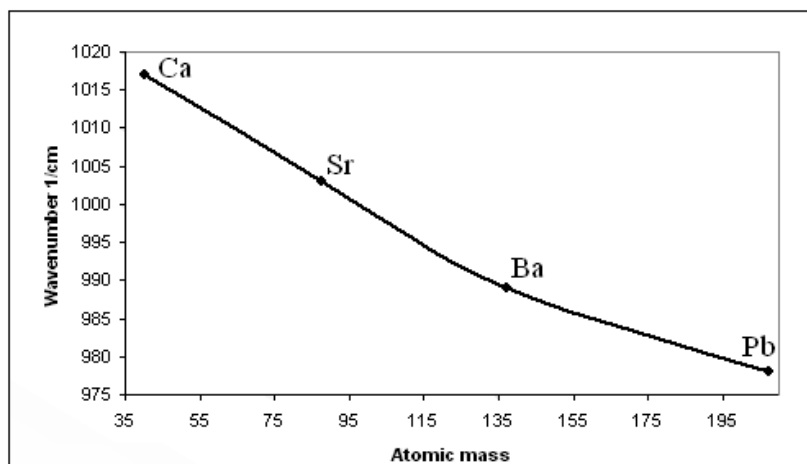


Fig. 3. Raman spectrum of the anhydrite

If we consider the Raman spectra of the barite group and the results presented above few considerations can be made: the wavenumber increases with an increase in the force; the stretching force constant between S-O for anhydrite it is $K = 6.41\text{ md/\AA}$ (Miyake et al., 1978); the wavenumber decreases with an increase of the atomic mass of the cations (Fig. 4).

Table 3. Raman bands in anhydrite (cm^{-1})

This study	Anhydrite		Assignments
	Liu et al., 2009	Bhagavantam, 1938	
235			Ca-O
419	416	415	ν_2
503	499	499	SO_4
	612	609	ν_4 SO_4
630	629	628	
678	676	674	
1017	1017	1018	$\nu_1 \text{SO}_4$
	1110		ν_3 SO_4
1129	1128	1128	
1160	1159	1160	
3395			$\nu(\text{H}_2\text{O})$

Fig. 4. Wavenumbers of the ν_1 vibrational Raman mode vs. Atomic mass of the cations

The Raman spectrum of the arcanite (Fig. 5), has the strongest intensity band at 985 cm^{-1} , which was assigned to the symmetric stretching mode ν_1 of SO_4 tetrahedra. The ν_2 mode (symmetric bending) appears at 457 cm^{-1} , the ν_3 mode (triply degenerate asymmetric stretching) at 1097 cm^{-1} , 1108 cm^{-1} and 1146 cm^{-1} . The ν_4 mode (asymmetric bending) was found at 622 cm^{-1} (Table 4).

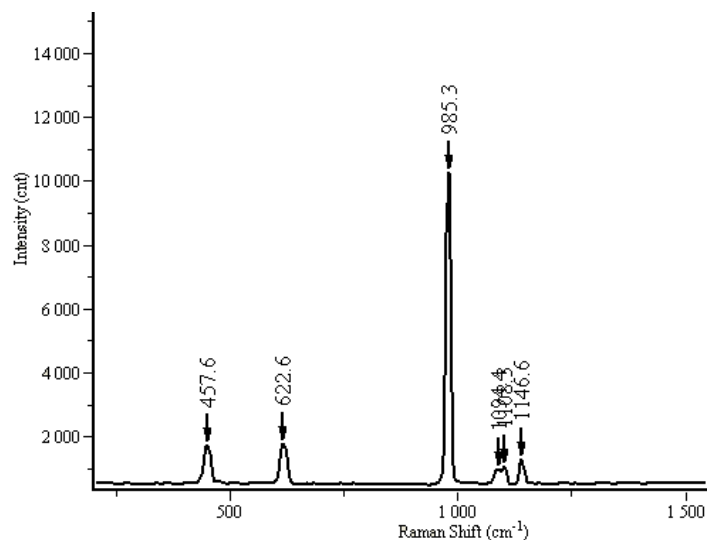


Fig. 5. Raman spectrum of the arcanite

Table 4. Raman bands of arcanite

Arcanite		Assignments
This study	Montero et al, 1974	
	453	ν_2
457	457	SO ₄
	617	ν_4
622	622	SO ₄
985	983	ν_1 SO ₄
1094	1093	ν_3 SO ₄
1108	1109	
	1110	
1146	1145	

Raman spectrum of CuSO₄ (Fig. 6) shows two strong bands at 1013 cm⁻¹ and 1045 cm⁻¹ which, were ascribed to the ν_1 modes of the two sulfate groups (doubly degenerate mode). The bands at 423 cm⁻¹, 448 cm⁻¹, 480 cm⁻¹ and 514 cm⁻¹ have been assigned to ν_2 sulfate mode (of two sulfate groups), the bands at 1101 cm⁻¹ and 1205 cm⁻¹ to the ν_3 mode and the bands at 622 cm⁻¹ and 670 cm⁻¹ to ν_4 mode of SO₄. The bands at 250 cm⁻¹, 269 cm⁻¹ and 347 cm⁻¹ have been assigned to the vibrations of Cu-O bonds.

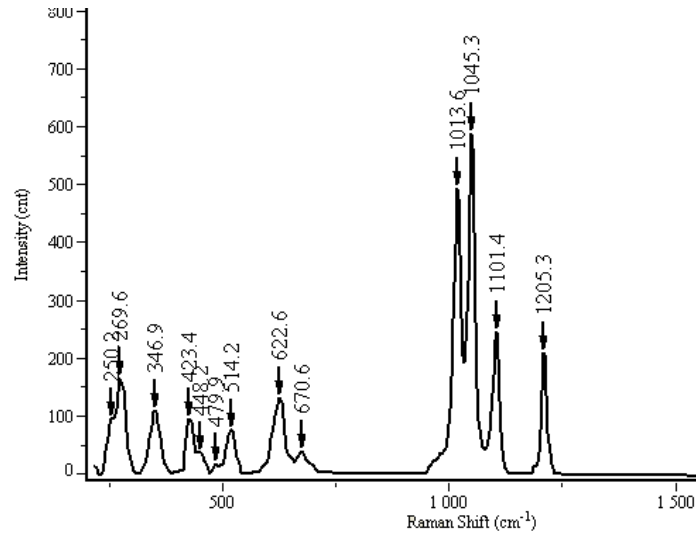


Fig. 6. Raman spectrum of the chalcocyanite

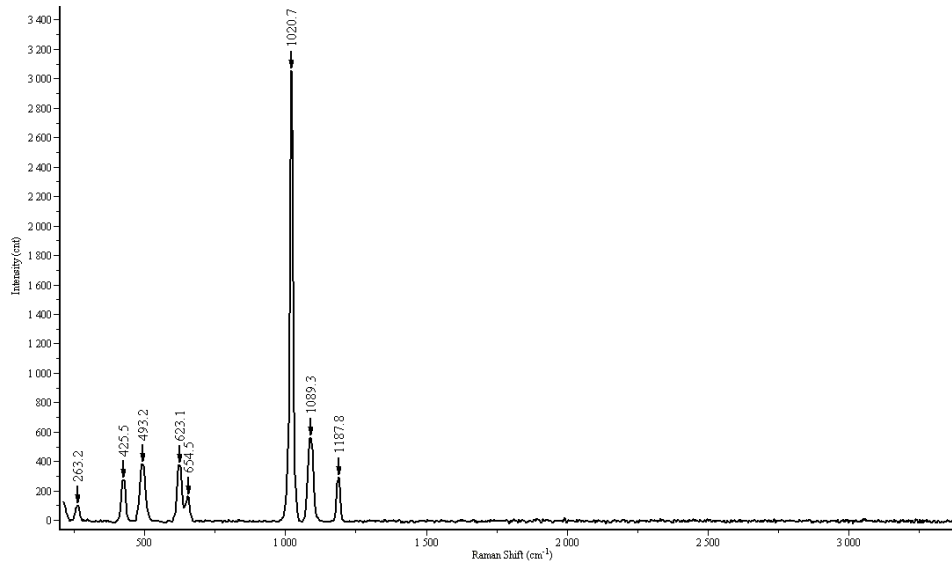


Fig. 7. Raman spectrum of the szmikite

The intense ν_1 symmetric stretching mode of the SO_4 from szmikite was found at 1021 cm^{-1} (Fig. 7). For ν_2 symmetric bending mode, the bands were found at 425 cm^{-1} and 493 cm^{-1} . The bands at 1089 cm^{-1} and 1189 cm^{-1} have been interpreted to represent the ν_3 asymmetric stretching mode, and the bands at 623 cm^{-1} and 654 cm^{-1} have been interpreted to represent the ν_4 asymmetric bending mode. The translational motions between the metal cation and the water molecule were observed in the Raman spectrum at the wavenumber value 263 cm^{-1} .

The syngenite Raman spectrum (Fig. 8) is governed by two strong bands at 982 cm^{-1} and 1006 cm^{-1} , that can be assigned to the ν_1 symmetric stretching modes of two sulfate groups. The bands at 1084 cm^{-1} , 1120 cm^{-1} , 1143 cm^{-1} and 1167 cm^{-1} can be ascribed to the splitting of the ν_3 mode of both sulfate groups. The ν_2 mode is present at 442 cm^{-1} , 477 cm^{-1} and 495 cm^{-1} . The sulfate ν_4 mode can be observed at 641 cm^{-1} and 663 cm^{-1} . The O-H stretching modes have been found at 3305 cm^{-1} and the vibration of the (M, H_2O) at 240 cm^{-1} (Table 5).

Table 5. Raman bands for syngenite (cm^{-1})

Syngenite		Assignments
This study	Kloprogge et al., 2002	
240		T(M, H_2O)
	424	ν_2 (SO_4)
442	441	
477	471	
495	491	
641	641	ν_4 (SO_4)
663		
982	981	ν_1 (SO_4)
1006	1004	
1084		ν_3 (SO_4)
1120	1117	
1143	1138	
1167	1166	
3305		ν (H_2O)

B. Acid sulfates

Linarite

The Raman spectrum of linarite (Fig. 9) is characterized by an intense band at 967 cm^{-1} attributed to the ν_1 mode of the sulfate group. The bands at 437 cm^{-1} , 465 cm^{-1} and 518 cm^{-1} were assigned to the ν_2 vibrational mode, the 1143 cm^{-1} band to the ν_3 mode; and the 613 cm^{-1} and 634 cm^{-1} ν_4 asymmetric bending to the ν_4 mode (Table 6).

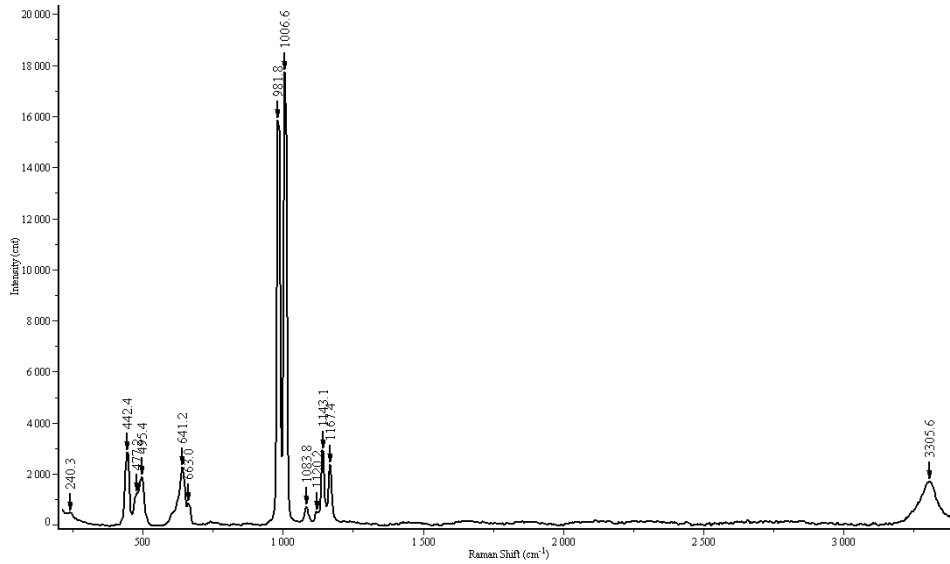


Fig. 8. Raman spectrum of the syngenite

A weak band that appears at 1021 cm^{-1} was assigned to the ν_3 mode. The linarite spectrum presents other bands at: 232 cm^{-1} , 347 cm^{-1} and 366 cm^{-1} due to Cu-OH/ Pb-OH vibrations and at 819 cm^{-1} due to the possible deformation of the O-H bond.

Table 6. Raman bands of linarite

Linarite		Assignments
This study	Lasnier, 1991	
232	230	M-OH
347	345	
366	370	
437	430	ν_2 (SO ₄)
465	460	
518	505	ν_4 (SO ₄)
613	612	
634	630	
819		OH bending
967	980	ν_1 (SO ₄)
1021	1030	ν_3 (SO ₄)
1143	1140	

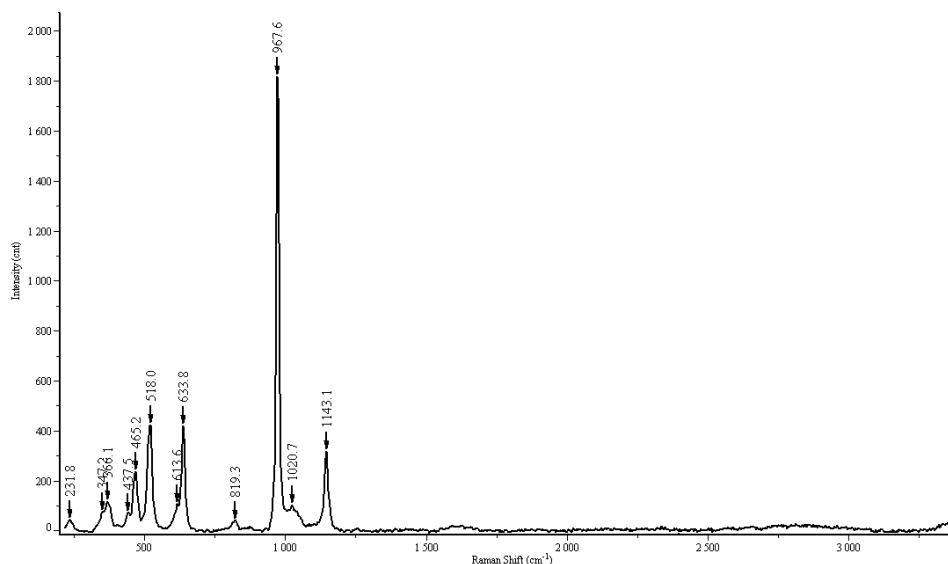


Fig. 9. Raman spectrum of the linarite

C. Hydrated Sulfates

1. Gypsum

The Raman spectrum of gypsum is presented in Figure 10. Most of the peaks show similar values with those found in the literature (Table 7).

The strongest Raman spectrum of gypsum was found at 1010 cm^{-1} and corresponds to the ν_1 symmetric stretch vibration mode of the SO_4 tetrahedra. Gypsum exhibits doublet for ν_2 symmetric bending, at 416 cm^{-1} and 495 cm^{-1} . The peak at 1143 cm^{-1} was assigned to the ν_3 asymmetric stretch vibration mode, and the peaks at 622 cm^{-1} and 674 cm^{-1} to the ν_4 asymmetric bending vibration modes. Another band that appears at 316 cm^{-1} has been assigned to the translational modes $T(\text{H}_2\text{O}, \text{Ca})$ (Sarma et al., 1998).

Figure 10 shows a comparison between the gypsum and anhydrite spectra. It can be observed that the internal modes frequencies of SO_4 group are similar. In anhydrite the ν_3 mode is split in two bands and can be explained by the distortion of SO_4 tetrahedra. The oxygen atoms of SO_4 groups are in different crystallographic environments. In gypsum, they are coordinated with a calcium atom and two water molecules, and in anhydrite with two calcium atoms. Therefore, the changes in the vibrational modes of the sulfate group could be a consequence of the dehydration process (Sarma et al., 1998). In other words, the wavenumbers of the bands increase with a decrease of the hydration degree, from gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) to anhydrite (CaSO_4) (Table 7).

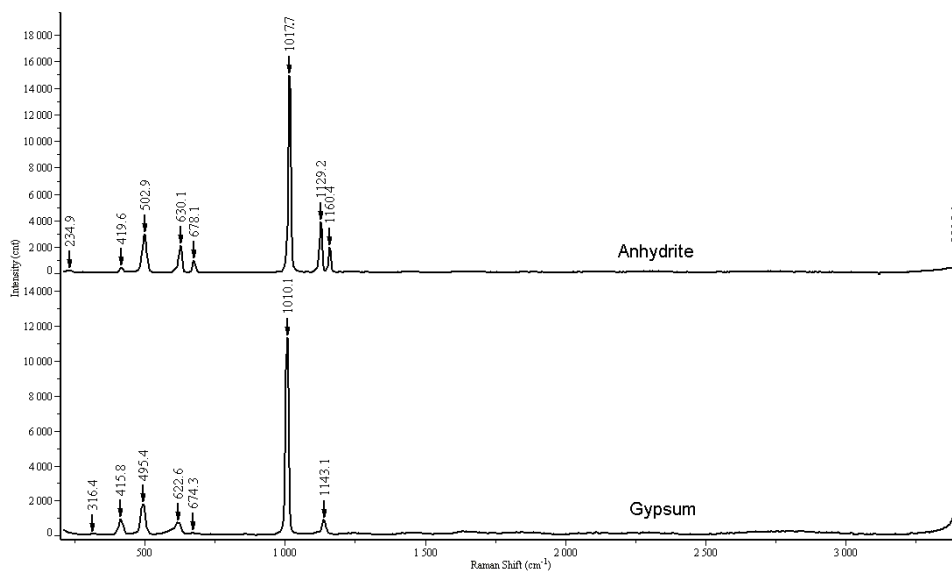


Figure 10. Raman spectra of gypsum and anhydrite

Because the measurements were made in the spectral range 200 – 3400 cm^{-1} , we could not see the characteristic bands for the stretching vibration modes of water in gypsum. They have been reported in literature at values of 3406 cm^{-1} and 3494 cm^{-1} (White, 2008).

Table 7. Raman bands of anhydrite, bassanite and gypsum (cm^{-1})

Anhydrite This study	Bassanite (Liu et al., 2009)	Gypsum		Assignments
		This study	White, 2008	
235				T(H ₂ O, Ca)
		316		
419	427	416	415	v ₂ (SO ₄)
503	489	495	494	
630	628	622	620	v ₄ (SO ₄)
678	668	674	671	
1017	1015	1010	1008	v ₁ (SO ₄)
1129	1128	1143	1136	
1160				v ₃ (SO ₄)

2. Melanterite, bieberite, epsomite and goslarite – $MSO_4 \cdot 7H_2O$

The Raman spectra of $FeSO_4 \cdot 7H_2O$ (melanterite) and $CoSO_4 \cdot 7H_2O$ (bieberite) are shown in Figures 11 and 12. The most intense Raman lines, corresponding to the ν_1 symmetric stretching vibration of the sulfate group were found at 992 cm^{-1} for melanterite and 1024 cm^{-1} for bieberite. The ν_2 mode of sulfate group was found at 457 cm^{-1} and 480 cm^{-1} in ferrous sulfate, and at 423 cm^{-1} and 495 cm^{-1} in bieberite; the ν_3 mode presents lines at 1074 cm^{-1} and 1146 cm^{-1} , respectively at 1069 cm^{-1} and 1181 cm^{-1} . The peaks 611 cm^{-1} of melanterite, 623 cm^{-1} and 667 cm^{-1} of bieberite were assigned to the ν_4 mode. In both spectra we observe peaks corresponding to water stretching modes, at 3385 cm^{-1} for melanterite and above 3400 cm^{-1} for bieberite. Chio et al., (2007) showed that increasing degrees of hydration, shift the intensity of the ν_1 peak to lower wavenumbers

In melanterite, the bands 214 cm^{-1} , 241 cm^{-1} and 285 cm^{-1} are attributed to the translational modes T (Fe, H_2O). In bieberite only two Raman bands appear, at 223 cm^{-1} and 285 cm^{-1} .

The melanterite spectrum shows some different band positions in Raman shift most probably due to analytical factors (Table 8).

Table 8. Raman bands for bieberite and melanterite (cm^{-1})

Bieberite	Melanterite		Assignments
	This study	Chio et al., 2007	
223	214	206	T(Fe, H_2O)
	241	241	
285	285	264	
423	457	446	ν_2 (SO_4)
495	480	465	
		565	ν_4 (SO_4)
623	611	619	
667			
875 917			ν (OH) ν (H_2O)
1024	992	976	ν_1 (SO_4)
1069	1074	1075	ν_3 (SO_4)
		1102	
1181	1146	1138	
		1625	ν (H_2O)
1801		1648	
	3385	3371	
		3436	

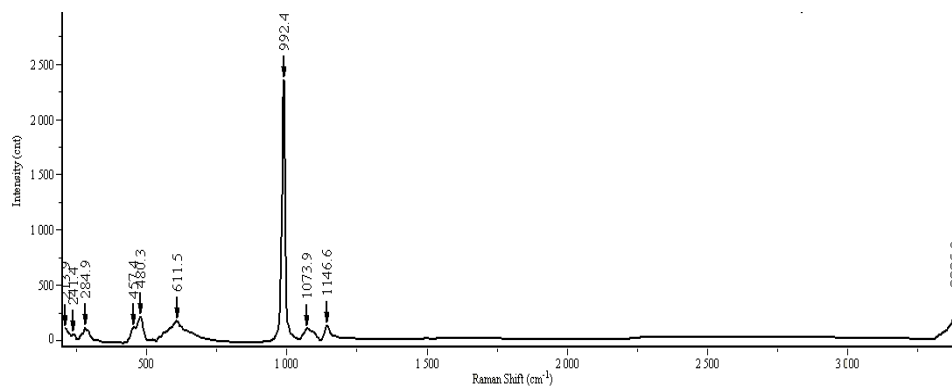


Fig.11. Raman spectra of the melanterite

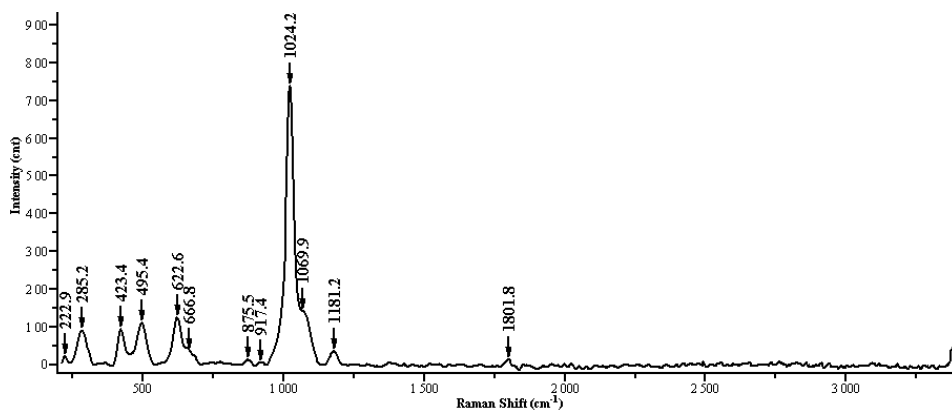


Fig. 12. Raman spectra of the bieberite

The Raman spectrum of epsomite (Fig. 13) shows an intense ν_1 vibration of SO_4 group at 985 cm^{-1} . The ν_2 mode appear at 469 cm^{-1} . Two bands, one at 1084 cm^{-1} and one at 1146 cm^{-1} have been assigned to the ν_3 mode and the band at 611 cm^{-1} to the ν_4 . The bands 246 cm^{-1} and 365 cm^{-1} were assigned to the vibrations of the Fe-O bond (where O is from H_2O). The vibration modes of water appear at 3397 cm^{-1} . In early studies, Lakshman (1941) reported for epsomite the vibrational modes of sulfate group and water molecule, and later, Shantakumari (1953) reported more bands, especially for water vibrations (Table 9).

In the case of goslarite, the Raman spectrum is more complex (Fig. 13). The characteristic bands for sulfate group vibrations were found at: 1024 cm^{-1} for the ν_1 mode; at 423 cm^{-1} and 510 cm^{-1} for the ν_2 mode; at 1084 cm^{-1} and 1191 cm^{-1} for the ν_3 mode and at 626 cm^{-1} and 671 cm^{-1} for the ν_4 mode. The peaks from the lower region of the spectrum, at the 223 cm^{-1} and 281 cm^{-1} , were attributed to the translational modes of the cation with the oxygen from water. The band 1492 cm^{-1} was assigned to the ν_2 bending mode of water molecule. Modes of O-H stretching were not observed in this study. The band at the wavenumber 913 cm^{-1} was attributed to vibrational modes of water molecules (Berger, 1976; Chio et al., 2007). The Raman spectra obtained in this study (Table 9) is very different from those mentioned in the literature (Shantakumari, 1953).

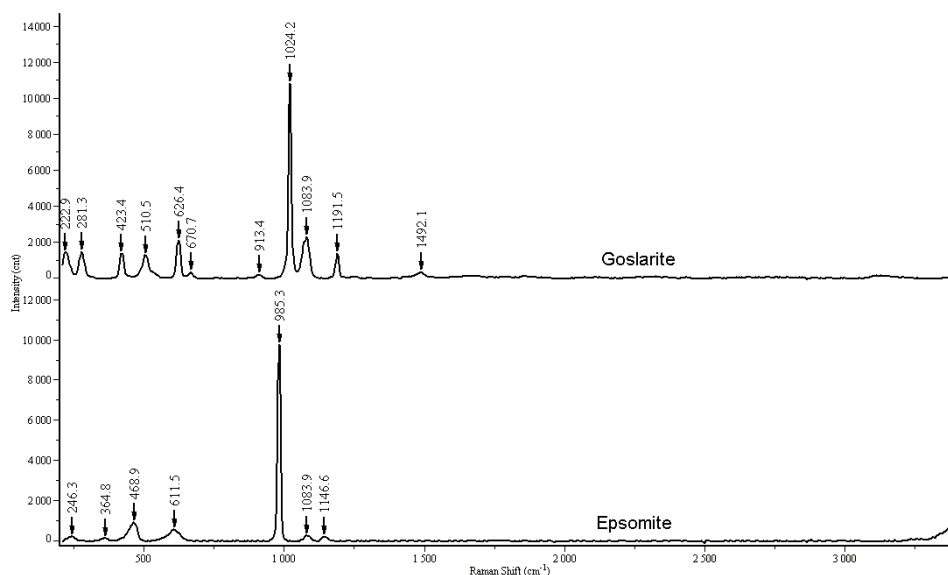


Fig. 13. Raman spectra of goslarite and epsomite

Conclusions

In all spectra were observed the four fundamental vibration modes of SO_4 tetrahedra, with variations in band positions and splitting, caused by the influences of the different metal cations. The vibration modes of the cation-oxygen bonds, except for the barite group minerals and arcanite were also measured.

Table 9. Raman bands of epsomite and goslarite (cm^{-1})

Epsomite			Goslarite		Assignments
This study	Lakshman, 1941	Shantakumari, 1953	This study	Shantakumari, 1953	
246		252	223	252	T(M, H ₂ O)
365		303	281	373	
		445	423	445	v ₂ (SO ₄)
469	455	461	510	461	v ₄ (SO ₄)
611	613	609	626	609	
		620	671	620	v(H ₂ O)
			913		
985	981	986	1024	990	v ₁ (SO ₄)
	1046	1059		1057	v ₃ (SO ₄)
		1064	1084	1062	
1084		1076		1094	
	1101	1098		1121	
		1134		1141	
1146		1148	1191		
			1492		v(H ₂ O)
		3185		3154	
	3226	3228			
	3285	3338		3342	
3397		3406		3436	
	3458	3446			
		3485		3512	

The measured Raman bands are similar to those reported in literature but melanterite and goslarite show certain differences. These differences were probably caused by the instruments and techniques. Water vibration modes do not appear in all hydrated sulfates used in the study (gypsum and goslarite), probably due to the spectral range 200 – 3400 cm^{-1} and the fact that water modes are observed in generally at wavenumbers higher than 3400 cm^{-1} . An interesting aspect is that in the spectrum of anhydrite was observed o band at 3395 cm^{-1} , which can be explained by the vibration mode of water absorbed from air on the crystal surface.

In the case of sulfates with similar structure (barite group), the wavenumber of the vibrational modes of SO₄ tetrahedra, decreases with an increase of the atomic mass of the metal cations. This characteristic does not appear in the case of hydrated sulfates, with different hydration degree. Also, Raman peaks shift to higher wavenumbers with an increase of the stretching force constant of S-O bonds.

For hydrated sulfates, the higher peak, corresponding to the symmetric stretching of SO_4 , shifts to lower vibrational wavenumbers with the increasing hydration.

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