

Investigations of the Fe sulfosalts berthierite, garavellite, arsenopyrite and gudmundite by Raman spectroscopy

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ABSTRACT

Arsenopyrite (FeAsS), gudmundite (FeSbS) and the rarer Fe sulfosalts berthierite (FeSb₂S₄) and garavellite (FeSbBiS₄), were investigated by Raman spectroscopy. Whereas (Sb,Bi)S₃ pyramids are responsible for the Raman spectra of berthierite and garavellite, the spectra of gudmundite and arsenopyrite arise from the stretching and bending modes of (Sb,As)S units. Internal vibrations for berthierite and garavellite occur between 400 and 50 cm⁻¹, and those of the gudmundite and arsenopyrite between 500 and 100 cm⁻¹. The longer bond distances of the SbS₃ groups readily explain the lower frequencies for berthierite in comparison with garavellite. Similarly, the greater mass and the longer bond distances of the Sb–S units also explain the lower frequencies observed for gudmundite relative to arsenopyrite.

KEYWORDS: arsenopyrite, berthierite, garavellite, gudmundite, Raman spectroscopy.

Introduction

THE mineral gudmundite (FeSbS) and the Fe sulfosalts berthierite (FeSb₂S₄) and garavellite (FeSbBiS₄) are relatively rare. In contrast, arsenopyrite (FeAsS) is common in various types of sulfide deposit and may constitute a major ore mineral in some deposits, especially orogenic gold ores.

The pyramidal XS₃ group (X = Sb, Bi) is responsible for the Raman and infrared (IR) spectroscopic features of berthierite and garavellite. Raman-allowed modes of gudmundite and arsenopyrite can be described as stretching and bending modes of (Sb,As)S units. Despite the work that has been done on the crystal structures of the minerals, Raman spectroscopic studies of berthierite, garavellite and gudmundite have not been published. Nevertheless, the RRUFF database project (Downs, 2006) contains unpolarized

Raman spectra of berthierite (#R070177), gudmundite (#R060741) and arsenopyrite (#R050071, #R061082, #R070585). There exist only a few papers dealing with Raman and IR spectroscopy of arsenopyrite (Lutz *et al.*, 1983; Mernagh and Trudu, 1993; McGuire *et al.*, 2001a,b; Giudici *et al.*, 2007).

The goal of the present work was twofold: (1) to investigate berthierite, garavellite, gudmundite and arsenopyrite by Raman spectroscopy; and (2) to examine the effects of the symmetry becoming lower on the pyramidal XS₃ groups (berthierite and garavellite) relative to isolated XS₃ pyramids of an ideal trigonal symmetry.

Crystallographic data

The crystal structure of berthierite (Fig. 1a) was first determined and refined by Buerger and Hahn (1955). Berthierite crystallizes in the space group *Pnma* with four formula units in the unit cell (Lukaszewicz *et al.*, 2001). The three-dimensional framework consists of two polyhedral types: FeS₆

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octahedra and SbS_3 pseudo-tetrahedra in which the empty vertex is occupied by the $5s^2$ lone pair of Sb^{3+} (Bente and Edenharter, 1989; Lemoine *et al.*, 1991; Lukaszewicz *et al.*, 2001). Sb1-S distances are in the range 2.49–2.60 Å whereas the Sb2-S bond lengths are in the range 2.42–2.51 Å (Lemoine *et al.*, 1991; Lukaszewicz *et al.*, 2001). By sharing two opposite edges, Fe octahedra form infinite $(\text{FeS}_4)_n^{6n-}$ chains running parallel to the c axis (Lemoine *et al.*, 1991) or the b axis (Lukaszewicz *et al.*, 2001). Sb^{3+} cations are inserted between the chains. Sb1 cations are attached to $(\text{FeS}_4)_n^{6n-}$ chains by short Sb1-S3 and Sb1-S4 bonds. The chains joined by Sb2 form layers perpendicular to c (Lukaszewicz *et al.*, 2001).

The garavellite structure ($Pnma$, $Z = 4$, Fig. 1a) was determined and refined by Bindi and Menchetti (2005). The arrangement of atoms in garavellite is the same as in berthierite (Buerger and Hahn, 1955; Gregorio *et al.*, 1979; Lemoine *et al.*, 1991; Lukaszewicz *et al.*, 2001); however, in garavellite the Sb2 position of berthierite is occupied fully by Bi^{3+} thus causing remarkable differences in the polyhedral configuration, especially in the Bi^{3+} coordination (Bindi and Menchetti, 2005). As in berthierite, FeS_6 octahedra are connected by edge-sharing to form infinite chains parallel to c . Sb and Bi atoms form, with the three nearest neighbours, SbS_3 and BiS_3 groups with a pseudo-tetrahedral configuration (Bindi and Menchetti, 2005). The empty vertex is occupied by the $5s^2$ and $6s^2$ lone pair of Sb^{3+} and Bi^{3+} , respectively, that lie in large, elongated pseudo-rectangular cavities. Sb-S distances are in the range 2.38–2.96 Å, whereas the Bi-S bond lengths are in the range 2.64–3.08 Å (Bindi and Menchetti, 2005). SbS_3 and BiS_3 groups are connected to the Fe octahedra in a different way, as the SbS_3 group shares two edges with as many FeS_6 octahedra of the same chain (Bindi and Menchetti, 2005). The BiS_3 group connects, by corner-sharing, three different FeS_6 octahedra of two adjacent chains (Bindi and Menchetti, 2005).

The crystal structure of gudmundite and arsenopyrite projected along the c axis is shown in Fig. 1b. All the structures of the gudmundite-arsenopyrite-pyrite-marcasite family are characterized by 3D polymerization of FeA_6 ($A = \text{S}, \text{As}, \text{Sb}$) octahedra, and all the anions form A_2 pairs (Strunz and Nickel, 2001). The crystal structure of gudmundite was determined and refined by Buerger (1939). Gudmundite crystallizes in the

space group $P2_1/c$ with $Z = 8$ (Anthony *et al.*, 2000).

After the first structural study by Buerger (1936), a detailed crystal-chemical study of arsenopyrite was performed by Morimoto and Clark (1961). More recently, Fuess *et al.* (1987) and Bindi *et al.* (2012) carried out new refinements on various samples of arsenopyrite. It crystallizes in space group $P2_1/c$ with $Z = 4$. In the structure of gudmundite and arsenopyrite, Fe atoms are coordinated octahedrally by three S and three Sb/As atoms. The FeSb_3S_3 and the FeAs_3S_3 octahedra in gudmundite and arsenopyrite, respectively, share two opposite edges to form single strips parallel to $[101]$, with alternating short and long Fe-Fe bonds (Fuess *et al.*, 1987; Bindi *et al.*, 2012).

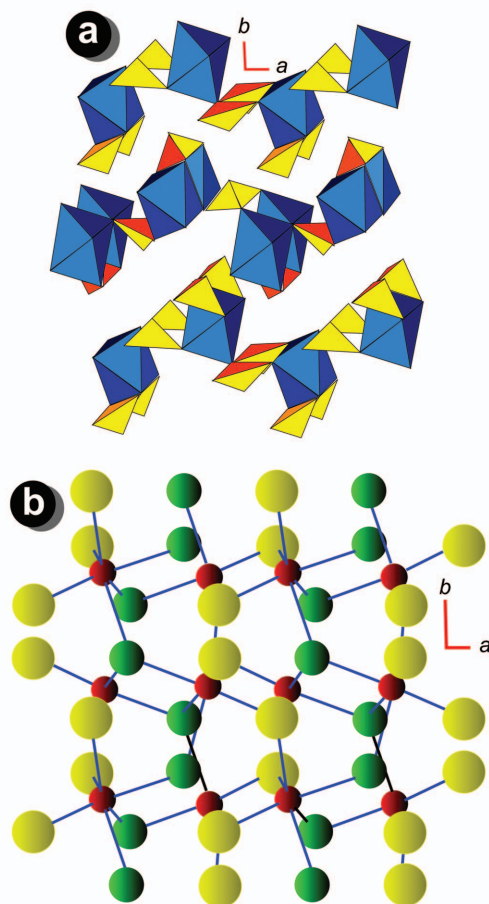


FIG. 1. Crystal structure of (a) berthierite and garavellite and (b) gudmundite and arsenopyrite.

Samples and experimental

The naturally occurring berthierite samples were from the Zlatá Baňa deposits, eastern Slovakia. The garavellite and gudmundite samples were from the Malé Karpaty Mountains, Western Carpathians, Slovakia and the arsenopyrite samples were from the Nistru mine, Maramures, Romania.

Carefully chosen samples were cut with a low-speed diamond saw and were ground with 600 and 1000 mesh silicon carbide on glass and polished with diamond paste (6, 3, 1 μm) on cloth to obtain a scratch-free surface.

Mineral compositions were obtained using polished thin sections by a Cameca SX 100 electron microprobe. Excitation voltage was 20 kV and beam current 15 nA. Elements were measured with a counting time between 10 and 20 s. Calibrations were performed using natural and synthetic reference materials.

The minerals investigated were characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 30 mA). Samples were measured in step scan mode with steps of $0.02^\circ 2\theta$ and a scan speed of $2^\circ 2\theta/\text{min}$ from 5 to $75^\circ 2\theta$. The analyses were performed on powder samples obtained from the polished sections after microprobe and Raman measurements had been carried out.

Raman spectra of all minerals were measured using backscatter geometry (180° configuration) at room temperature, in the range from 1000 to 50 cm^{-1} using a LabRAM-HR (Horiba Jobin-Yvon RPA-HE 532) spectrophotometer, equipped with an electrically cooled CCD detector and an Olympus BX-41 microscope. The 532 nm line at 210 mW of a frequency-doubled Nd-YAG laser (attenuated to 10%) was used for excitation. Exciting radiation with the power densities of $8.5 \times 10^{-3} \text{ mW } \mu\text{m}^{-2}$ and polarization extinction $>500:1$ was focused on the sample surface with a $100\times/0.9$ Olympus objective to a spot area $\sim 0.5 \text{ } \mu\text{m}^2$. The laser was defocused slightly to avoid sample damage. Backscattered radiation was analysed with a 1200 mm^{-1} grating monochromator. Raman intensities were collected with a multichannel air-cooled (-70°C) open electrode front-illuminated CCD detector (1024×256 pixels, pixel size $26 \text{ } \mu\text{m} \times 26 \text{ } \mu\text{m}$). The resolution of the system was $1\text{--}2 \text{ cm}^{-1}$ and accuracy of frequency was $\pm 1 \text{ cm}^{-1}$ (both calibrated with the Rayleigh line and the

520.5 cm^{-1} line of a Si standard). Reflected and Rayleigh scattered photons, which represent the main source of interference, were removed by a holographic notch filter specific to the laser energy. Because only relative changes of the band widths were investigated, a mathematical correction of the full width at half maximum (FWHM) values for the apparatus function (Irmer, 1985; Verma *et al.*, 1995) was not applied. Instrument control, data acquisition and baseline corrections were carried out with LabSpec 5 (Horiba Jobin-Yvon). Depending on the signal intensity, accumulations with 10–20 min per ‘spectroscopic window’ (i.e. exposure time of the detector) were measured. In order to check sample homogeneity, several spectra (8–10) were acquired on the same sample. Peak centres of single bands were determined by fits of combined Gaussian amplitude functions using *PeakFit* 4.12 software (Jandel Scientific).

Results

Sample characterization

The samples were examined qualitatively by ore microscopy. Berthierite forms light- to pinkish-grey needle-shaped crystals or anhedral aggregates. Garavellite forms small irregular aggregates of anhedral crystals. In reflected light garavellite is grey with a brown-olive tint similar to tetrahedrite. Bireflectance is distinct, whereas anisotropy is strong with colours in 45° positions from yellowish grey to bluish grey. Gudmundite occurs as irregular or rounded grains in aggregates. Gudmundite is white, has a high reflectivity and is slightly bireflective. Arsenopyrite occurs as euhedral grains, anhedral aggregates and several-mm-thick veinlets. The samples show no compositional zoning or microscopic inclusion of other minerals. Chemical analyses (Table 1) and XRD data confirm the homogeneity and the identity of the samples studied, respectively. Except for garavellite (Fig. 2), XRD patterns of the minerals investigated can be found in the *American Mineralogist* Crystal Structure Database (<http://ruff.geo.arizona.edu/AMS/amcsd.php>). The chemical compositions of the minerals correspond closely to the ideal structural formulae. Based on seven atoms per formula unit, berthierite and garavellite have the formulae $\text{Fe}_{1.02}(\text{Sb}_{1.99}\text{As}_{0.02})_{2.01}\text{S}_{3.97}$ and $(\text{Fe}_{0.96}\text{Zn}_{0.02})_{0.98}(\text{Bi}_{0.94}\text{Sb}_{1.11}\text{As}_{0.01})\text{S}_{3.99}$, respectively; gudmundite and arsenopyrite, calculated on the basis of three atoms per

TABLE 1. Chemical analyses of the minerals investigated (each analysis represents one grain).

Fe	Sb	As	Au	S	Total	Fe	Zn	Sb	As	Bi	S	Total
Berthierite						Garavellite						
12.80	55.86	0.11	—	29.05	97.82	9.81	0.05	24.14	0.10	40.80	25.08	99.98
12.99	55.54	0.33	—	29.16	98.02	10.27	0.21	26.40	0.09	38.49	25.09	100.55
12.69	55.47	0.34	—	29.12	97.62	9.88	0.33	26.61	0.13	41.74	24.50	103.19
12.55	55.61	0.33	—	29.63	98.12	9.86	0.09	25.68	0.12	38.78	25.83	100.36
12.53	56.22	0.29	—	29.74	98.78	10.36	0.16	24.87	0.02	40.62	24.91	100.94
Arsenopyrite						Gudmundite						
35.48	—	41.68	0.05	23.02	100.23	26.74	—	57.47	0.04	—	15.51	99.76
35.62	0.02	41.77	0.18	23.01	100.60	26.44	—	58.11	—	—	14.73	99.28
35.33	—	42.54	0.07	22.93	100.87	26.68	—	58.13	0.01	—	15.24	100.06
34.33	0.06	41.96	—	22.13	98.48	26.71	—	57.10	0.03	—	15.13	98.97
34.46	0.07	42.08	0.11	21.28	98.00	25.92	—	57.26	—	—	14.75	97.93

formula unit, give the formulae $\text{Fe}_{1.01}\text{As}_{0.91}\text{S}_{1.08}$ and $\text{Fe}_{1.02}\text{Sb}_{0.92}\text{S}_{1.06}$, respectively.

dominate the spectrum (Fig. 5). Peak fitting reveals a total of 17 bands and shoulders with different intensities (Fig. 5).

Raman spectra of berthierite and garavellite

In the berthierite spectrum, bands occur in the region between 400 and 50 cm^{-1} with no additional bands at higher frequencies (Fig. 3). The Raman spectra of berthierite (Fig. 4) can be divided into two groups of bands, i.e. those between 400–200 cm^{-1} and those at 150–50 cm^{-1} . In the first region (>200 cm^{-1} , Fig. 4), a group of very weak to very sharp distinct bands and shoulders are readily observed. Band deconvolution of the berthierite spectrum reveals eight bands in this region. The second region shows seven peaks and shoulders (Fig. 4).

In the garavellite spectrum, bands occur in the region between 400 and 50 cm^{-1} with no additional bands at higher frequencies (Fig. 3). Two prominent strong bands at 338 and 214 cm^{-1}

Raman spectra of gudmundite and arsenopyrite

In the gudmundite spectrum, bands occur between 500 and 100 cm^{-1} with no additional bands at lower or higher frequencies (Fig. 3). A sharp, distinct and very strong band at 305 cm^{-1} and two strong bands at 288 and 152 cm^{-1} are observed (Fig. 6). Peak fitting reveals a total of 17 bands (Fig. 6).

The arsenopyrite spectrum (Fig. 3) is substantially different from the spectra found in the literature (Mernagh and Trudu, 1993; McGuire *et al.*, 2001b) or in the RRUFF database (Downs, 2006). However, it shows great similarity to the #R070585 spectrum in RRUFF database (Downs, 2006). The differences in spectra may be attributed to oriented measurements (e.g.

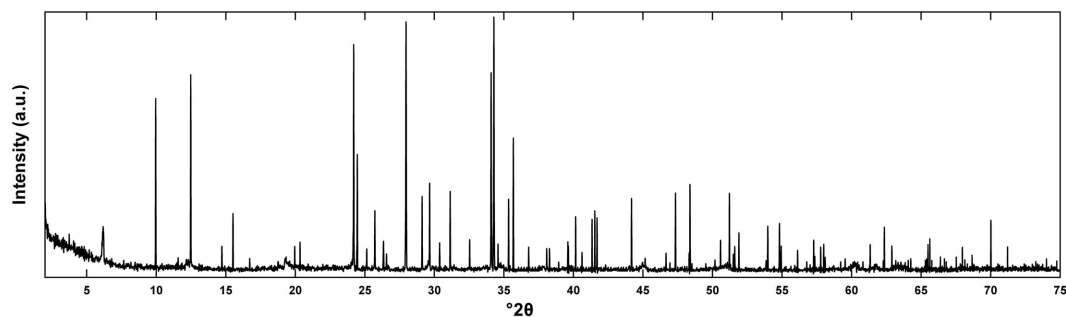


FIG. 2. XRD pattern of garavellite.

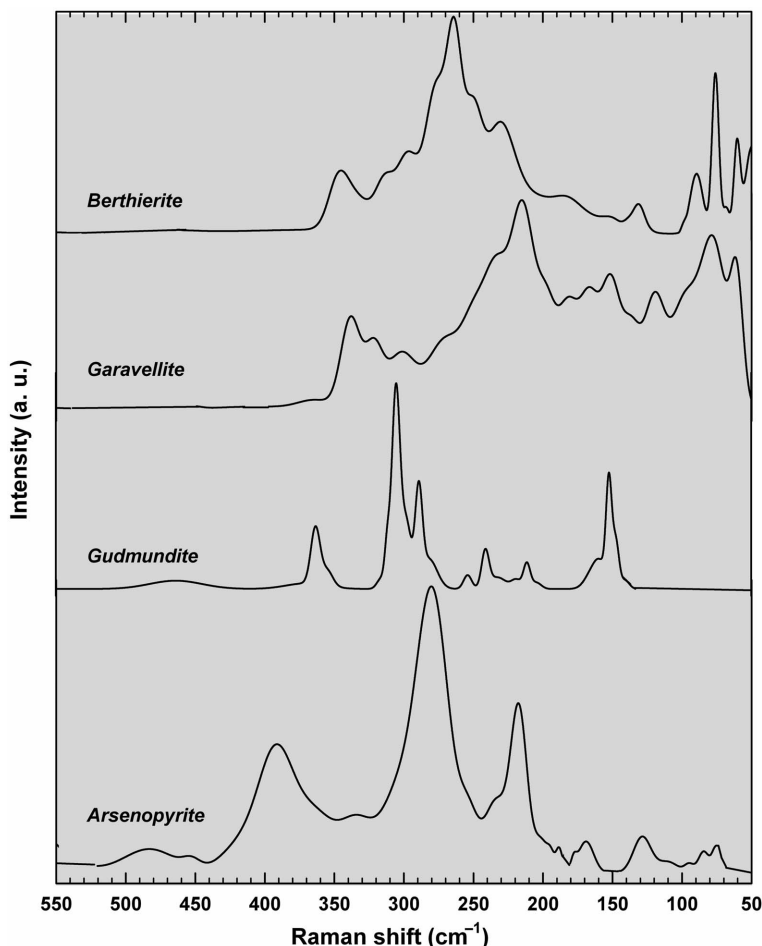


FIG. 3. Raman spectra of the minerals investigated.

#R050071; Downs, 2006), sample burning (e.g. #R061082; Downs, 2006) or to treating samples with HCl (McGuire *et al.*, 2001*b*). In the spectrum of arsenopyrite, bands appear in the region between 500 and 100 cm^{-1} . The spectrum is characterized by a very strong and relatively broad band at 280 cm^{-1} and two strong to medium bands at 392 and 217 cm^{-1} (Fig. 7). Band deconvolution of the arsenopyrite spectra reveals 12 weak to very weak vibrational modes (Fig. 7).

Discussion

Raman bands of berthierite and garavellite occur between 400 and 50 cm^{-1} (Figs 4, 5, Table 2), whereas those of gudmundite and arsenopyrite appear between 500 and 100 cm^{-1} (Figs 6, 7, Table 2), with the low-energy limit determined

only by the cut-off values of the Raman notch and edge filters.

Berthierite and garavellite are expected to show the characteristic vibrational modes of XS_3 ($X = \text{Sb, Bi}$) groups and further lattice modes of the mineral constituents. Raman-allowed modes of gudmundite and arsenopyrite can be described as stretching and bending modes of the $(\text{Sb,As})\text{S}$ units (see Fig. 1).

According to Nakamoto (1997), an isolated ideal pyramidal XY_3 group, which possesses ideal trigonal symmetry (C_{3v} point group), is expected to show only four normal modes of vibration ($2A_1 + 2E$). All four vibrational modes of the XY_3 pyramids are Raman- and IR-active, where the two stretching vibrations ν_1 (A_1) and ν_3 (E) and the two bending vibrations ν_2 (A_1) and ν_4 (E) overlap or are close in energy.

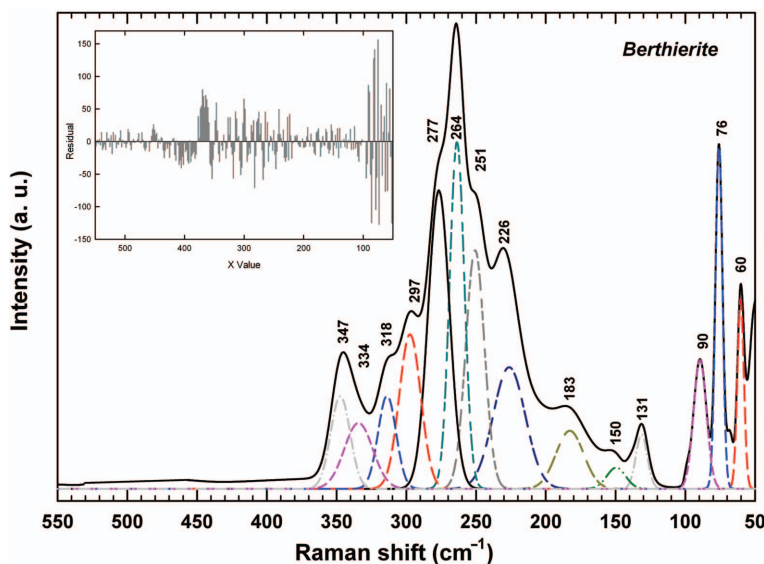


FIG. 4. The positions of the bands (cm^{-1}) of berthierite obtained by using the *PeakFit* program. (Goodness of fit (r^2) > 0.997), with the residuals vs. fitted values.

Positional parameters of gudmundite ($P2_1/c$, $Z = 8$) and arsenopyrite ($P2_1/c$, $Z = 4$) indicate that all atoms occupy $4(e)$. The primitive unit cell of gudmundite and arsenopyrite minerals contains 24 and 12 atoms, respectively. The number of allowable modes of gudmundite is 69 consisting of $18 A_g(\text{R}) + 18 B_g(\text{R}) + 17 A_u(\text{IR}) + 16 B_u(\text{IR})$,

whereas 33 are allowed for arsenopyrite, consisting of $9 A_g(\text{R}) + 9 B_g(\text{R}) + 8 A_u(\text{IR}) + 7 B_u(\text{IR})$.

Band assignments for berthierite and garavellite are based on the sequence of band energies given by Nakamoto (1997) with $\nu_1 > \nu_3 > \nu_2 > \nu_4$ and by comparison with the spectra of minerals

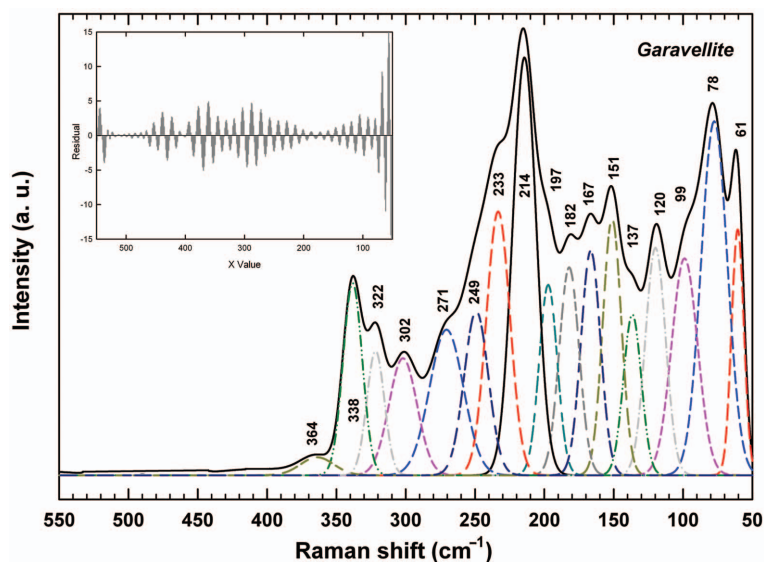


FIG. 5. The positions of the bands (cm^{-1}) of garavellite obtained by using the *PeakFit* program ($r^2 > 0.995$), with the residuals vs. fitted values.

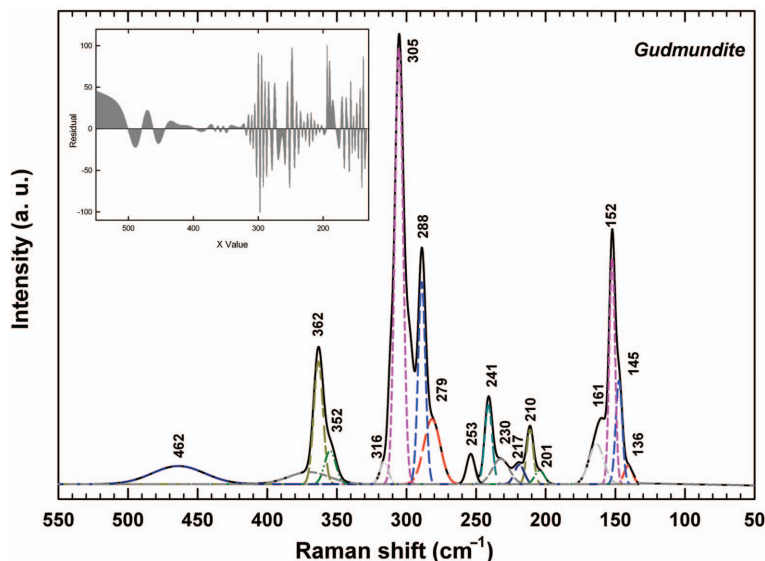


FIG. 6. The positions of the bands (cm^{-1}) of gudmundite obtained by using the *PeakFit* program ($r^2 > 0.996$), with the residuals vs. fitted values.

reported by Kharbush *et al.* (2007, 2009) and Kharbush (2011). Those for gudmundite and arsenopyrite are based upon the observations reported by Lutz *et al.* (1983), Mycroft *et al.* (1990), Lutz and Müller (1991), Mernagh and Trudu (1993), McGuire *et al.* (2001a,b) and Giudici *et al.* (2007).

The weak Raman band at 347 cm^{-1} in the berthierite spectrum (Fig. 4) is assigned to the ν_1 symmetric Sb–S stretching mode (Table 2). The very weak shoulder at 334 cm^{-1} is assigned to the ν_3 antisymmetric Sb–S stretching mode. The weak to medium shoulder and band at 318 and 297 cm^{-1} , respectively, are assigned to the ν_2

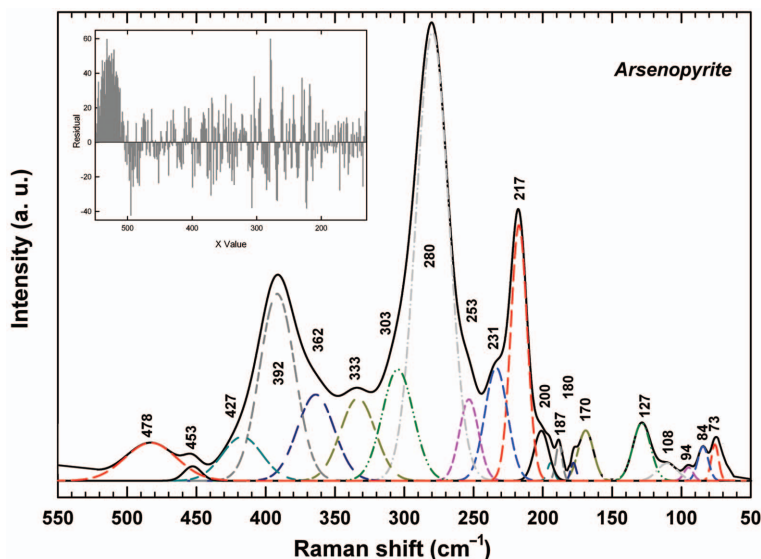


FIG. 7. The positions of the bands (cm^{-1}) of arsenopyrite obtained by using the *PeakFit* program ($r^2 > 0.998$), with the residuals vs. fitted values.

TABLE 2. Band positions (cm^{-1}) and assignments for the Raman spectra of the minerals investigated.

Vibrations	— Berthierite —		— Garavellite —		Vibrations	— Gudmundite —		— Arsenopyrite —	
	Band position (cm^{-1})	FWHM*	Band position (cm^{-1})	FWHM		Band position (cm^{-1})	FWHM	Band position (cm^{-1})	FWHM
Stretching	ν_1	347	16.34	28.23		462	44.10	478	43.83
	ν_3	334	24.01	16.29	S—S	241	6.28	427	33.75
						217	8.24	217	13.76
						152	4.78		
Bending	ν_2	318	15.20	14.96		362	7.78	453	14.80
		297	18.15	23.83		352	9.47	392	29.83
						316	7.06	362	31.30
	ν_4	277	17.98	28.63		305	6.88	333	29.53
		264	12.33	20.54		288	6.07	303	26.43
		251	15.69	19.98	(Sb,As)—S	279	13.83	280	27.39
		226	27.08	19.93		253	6.87	253	16.15
						230	14.16	231	19.13
Lattice modes		183	23.29	15.31		210	5.76	200	12.46
		150	15.75	16.87		201	8.19	187	5.40
		131	9.68	16.50		161	12.49	170	12.95
		90	13.35	15.63					
		76	10.83	15.14	(Sb,As)—Fe	145	5.49	127	14.95
		60	5.84	17.19		136	7.17	108	16.86
			5.50	22.03				94	7.81
				22.24				84	8.92
				10.44				73	6.24

* FWHM: The full width at half maximum, a parameter describing points on the curve at which the function reaches half its maximum value.

symmetric bending vibrations of the SbS_3 group. The dominant Raman band at 264 cm^{-1} and the weak to medium bands at 277 , 251 and 226 cm^{-1} are assigned to the ν_4 antisymmetric bending vibrations of the pyramidal SbS_3 group. The very weak, medium to strong bands and shoulders that occur below $\sim 200\text{ cm}^{-1}$, are assigned to lattice vibrational modes (Fig. 4, Table 2).

In the garavellite spectrum (Fig. 5, Table 2) the very weak intensity shoulder at 364 cm^{-1} is assigned to the symmetric (Sb,Bi)–S stretching mode, and the strong band at 338 cm^{-1} to the antisymmetric stretching modes. The doublet at 322 and 302 cm^{-1} is assigned to the symmetric bending modes, whereas the medium bands at 271 , 249 , 233 and 214 cm^{-1} are antisymmetric bending modes (Fig. 5, Table 2). In garavellite, absorption bands which are not related to stretching or bending modes of SbS_3 groups occur below $\sim 200\text{ cm}^{-1}$ (Fig. 5, Table 2).

Peaks at ~ 462 , 241 , 217 and 152 cm^{-1} and at 478 , 427 and 217 cm^{-1} in the gudmundite (Fig. 6, Table 2) and arsenopyrite (Fig. 7, Table 2) spectra, respectively, were attributed to vibrational modes of elemental sulfur (Mycroft *et al.*, 1990; McGuire *et al.*, 2001a,b). According to McGuire *et al.* (2001a,b) and Giudici *et al.* (2007), the bands that arise due to Fe–(As,Sb) vibrations occur below 150 cm^{-1} , whereas the phonon bands of bulk arsenopyrite appear as a series of broad features between 150 and 400 cm^{-1} . Therefore, the bands at 145 and 136 cm^{-1} in gudmundite and below 127 cm^{-1} in arsenopyrite were assigned to Fe–(Sb,As) vibrations. Other bands in the spectra of gudmundite and

arsenopyrite were considered to be due to (Sb–As)–S stretching and bending vibrations.

Although only four normal modes of vibration for the XS_3 group ($2A_1 + 2E$) should occur in the spectra of berthierite and garavellite (see above), both minerals show additional bands. The increase in the number of the bands can be related directly to the symmetry of the XS_3 pyramids. Because of intermolecular interactions, the symmetry of a molecule is generally lower in the crystalline state. Therefore, the vibrations of a molecule in the crystalline state are governed by a new selection rule derived from site symmetry (Nakamoto, 1997). In berthierite and garavellite the symmetry of the pyramidal XS_3 groups are reduced from C_{3v} symmetry to C_s site symmetry. As a result, the selection rules will be changed and the $2A_1 + 2E$ modes will translate or split into other modes (Table 3). Lowering the symmetry of the XS_3 pyramids (from C_{3v} to C_s) causes the two degenerate vibrations to split into four Raman- and IR-active bands (Table 3) (Nakamoto, 1997). Correlating the translated or splitting modes to the $Pnma$ space group of berthierite and garavellite will result in additional splitting or an increase in the number of these modes (Table 3). Furthermore, the increased number of bands is probably related to the presence of two crystallographically different $\text{Sb}(1)\text{S}_3$ and $\text{Sb}(2)\text{S}_3$ groups in berthierite and SbS_3 and BiS_3 pyramids in garavellite. This observation has been reported previously for stibnite, bismuthinite and kermesite by Kharbish *et al.* (2009) and for parapirotite, weissbergite and lorandite by Kharbish (2011). In addition, inspection of the structures of the

TABLE 3. Splitting pattern of the XS_3 vibrations (after Nakamoto, 1997).

Point/space group	Splitting pattern of the XS_3 modes					
	A_1		E			
C_{3v}	$\nu_1(A_1)$ ↓	$\nu_2(A_1)$ ↓	$\nu_3(E)$ ↓		$\nu_4(E)$ ↓	
C_s	$\nu_1(A')$ ↓	$\nu_3(A')$ ↓	$\nu_2(A)$ ↓	$\nu_5(A'')$ ↓	$\nu_4(A'')$ ↓	$\nu_6(A'')$ ↓
D_{2h}^{16}	A_g (R) B_{2g} (R) B_{1u} (IR) B_{3u} (IR)	A_g (R) B_{2g} (R) B_{1u} (IR) B_{3u} (IR)	A_g (R) B_{2g} (R) B_{1u} (IR) B_{3u} (IR)	B_{1g} (R) B_{3g} (R) A_u (IR) B_{2u} (IR)	A_g (R) B_{2g} (R) B_{1u} (IR) B_{3u} (IR)	B_{1g} (R) B_{3g} (R) A_u (IR) B_{2u} (IR)

R – Raman active; IR – Infrared active.

berthierite and garavellite (Fig. 1a) reveals that the XS_3 pyramids are interconnected *via* common S atoms, which may also increase the number of the bands. An increase in the number of bands due to the interconnection of the pyramidal XS_3 group was noted previously for many sulfosalts (Kharbish *et al.*, 2009; Kharbish, 2011).

According to the Hooke's law and the 'classical harmonic oscillator model', the frequency of vibrational modes is a function of the bond strength and the atomic mass of the atoms involved in the vibration. The peak location depends upon the interactions and the bonding behaviour among different atoms. The shift of the garavellite peaks to higher frequencies in comparison to those in berthierite can be attributed to differences in bond lengths (Fig. 8). Therefore, the shorter Sb–S bond lengths (~ 2.38 Å as recorded by Bindi and Menchetti, 2005) in garavellite result in peak blue shifts (to higher energy). The longer Sb–S bond lengths (~ 2.42 Å as recorded by Lemoine *et al.*, 1991 and Lukaszewicz *et al.* 2001 in berthierite effectively lower the bond energy (i.e. spreads the bonding energy over more space) and the peak will red-shift to lower frequencies.

The band blue shifts in arsenopyrite can be linked to the smaller mass of As atoms in comparison with Sb atoms in gudmundite and also to different bond lengths (Fig. 9). Thus, the shorter As–S bonds (2.346 Å or 2.374 Å, as recorded by Fuess *et al.* (1987) and Bindi *et al.* (2012), respectively) in arsenopyrite cause the

blue shift, in comparison with the longer Sb–S bonds (~ 2.928 Å, calculated) in gudmundite.

Comparison between the stretching and bending band positions and the X–S distances (Fig. 8) shows decreasing wavenumbers of the bands from tetrahedrite to garavellite, berthierite, bournonite, parapirotite, weissbergite and stibnite. In addition, they occur in the spectroscopic region $400\text{--}200 \pm 20 \text{ cm}^{-1}$ (Fig. 8), which is considered the characteristic region for sulfides (Wang *et al.*, 1994). The vibrational modes of the XS_3 pyramids in garavellite and berthierite should therefore be expected to occur in the region between 400 and $200 \pm 20 \text{ cm}^{-1}$ while the bands that occur below $200 \pm 20 \text{ cm}^{-1}$ can be assigned to the lattice modes.

More than one effect can contribute to Raman line-shape broadening with the same mineral. It is important to explain its behaviour as a response to different perturbations present in the mineral itself. For example Campbell and Fauchet (1986) reported that grain-size effects produce large shifts and a broadening of the Raman spectrum of silicon. However, such behaviour is beyond the scope of the present study.

A comparison between Raman line-shape broadening in similar modes is shown in Fig. 10. Molecules in excited states return rapidly to their ground state and this relaxation is called the lifetime (τ). The lifetime is inversely proportional to the FWHM and therefore a short τ leads to broad peaks and *vice versa*. This explains simply the difference in FWHM in similar modes

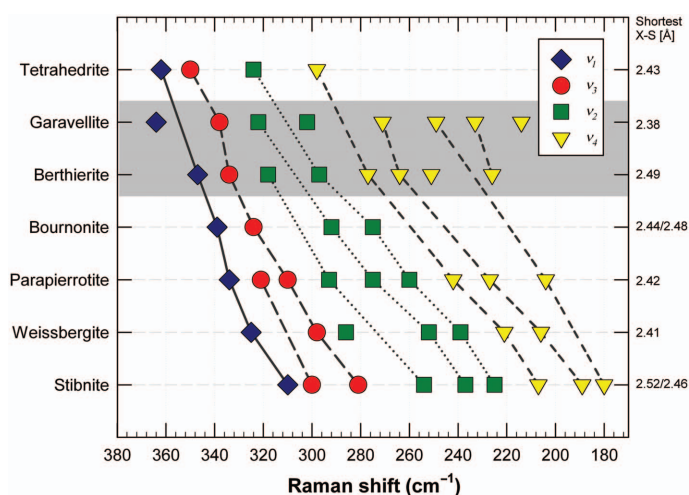


FIG. 8. Positions of the vibrational modes in berthierite and garavellite together with minerals containing XS_3 pyramids, data after Kharbish *et al.* (2007, 2009) and Kharbish (2011).

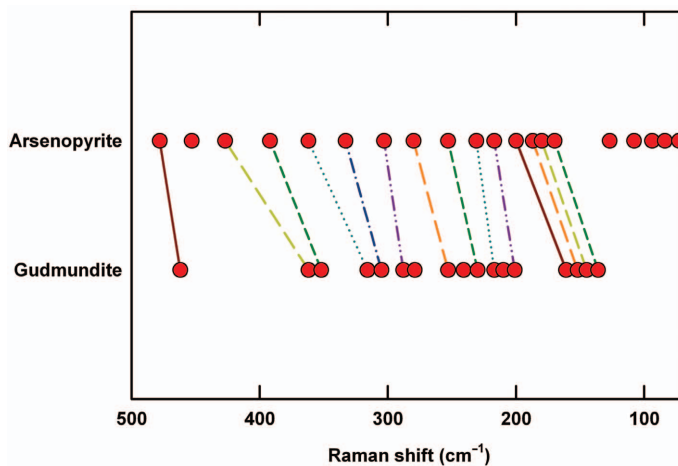


FIG. 9. Positions of the vibrational modes in gudmundite and arsenopyrite.

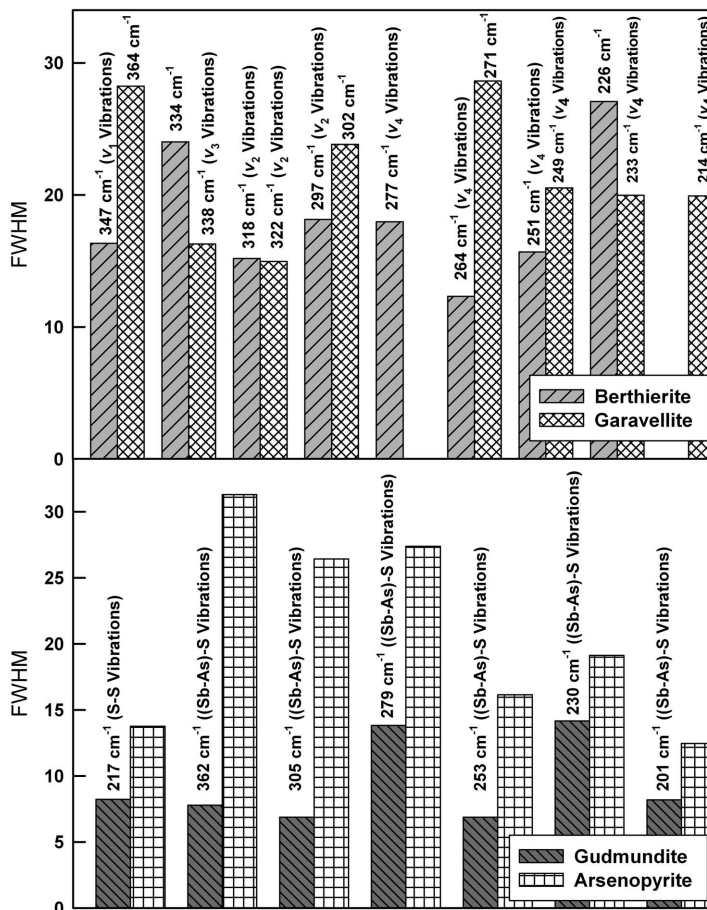


FIG. 10. Relation between band position and FWHM in the minerals investigated.

in berthierite–garavellite (Fig. 10) and in gudmundite–arsenopyrite (Fig. 10). Consequently, the longer bonds in berthierite and gudmundite may result in relatively narrow bands in comparison with garavellite and arsenopyrite, respectively (Fig. 10).

Conclusions

Fundamental stretching and bending vibrations of (Sb,Bi)S₃ groups and in (Sb,As)S units occur between 500 and 50 cm⁻¹ in the Raman spectra of berthierite and garavellite, and gudmundite and arsenopyrite, respectively. The appearance of the spectra changes continuously with composition. The greater mass and longer bond distances of Sb–S units also explain the lower frequencies of gudmundite vibrations relative to arsenopyrite. No striking differences in spectroscopic features are evident between minerals containing isolated and interconnected XS₃ groups. This behaviour is consistent with the spectroscopic features of e.g. orthosilicates and orthophosphates vs. polymerized silicates and phosphates (Nyquist and Kagel, 1971; Farmer, 1974).

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