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1 Vibrational spectroscopic study of the arsenate mineral
2 strashimirite $\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ - Relationship to other
3 basic copper arsenates

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11
12 **Abstract**

13
14 The basic copper arsenate mineral strashimirite $\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ from two
15 different localities has been studied by Raman spectroscopy and complemented by
16 infrared spectroscopy. Two strashimirite mineral samples were obtained from the
17 Czech (sample A) and Slovak (sample B) Republics. Two Raman bands for sample A
18 are identified at 839 and 856 cm^{-1} and for sample B at 843 and 891 cm^{-1} are assigned
19 to the ν_1 (AsO_4^{3-}) symmetric and the ν_3 (AsO_4^{3-}) antisymmetric stretching modes,
20 respectively. The broad band for sample A centred upon 500 cm^{-1} , resolved into
21 component bands at 467, 497, 526 and 554 cm^{-1} and for sample B at 507 and 560
22 cm^{-1} include bands which are attributable to the ν_4 (AsO_4^{3-}) bending mode. In the
23 Raman spectra, two bands (sample A) at 337 and 393 cm^{-1} and at 343 and 374 cm^{-1}
24 for sample B are attributed to the ν_2 (AsO_4^{3-}) bending mode. The Raman spectrum of
25 strashimirite sample A shows three resolved bands at 3450, 3488 and 3585 cm^{-1} . The
26 first two bands are attributed to water stretching vibrations whereas the band at 3585
27 cm^{-1} to OH stretching vibrations of the hydroxyl units. Two bands (3497 and 3444
28 cm^{-1}) are observed in the Raman spectrum of B. A comparison is made of the Raman
29 spectrum of strashimirite with the Raman spectra of other selected basic copper
30 arsenates including olivenite, cornwallite, cornubite and clinoclase.

31

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32 *Keywords:* Raman spectroscopy, infrared spectroscopy, strashimirite, olivenite,
33 clinoclase, cornwallite, arsenate minerals

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35

36 **1. Introduction**

37

38 The mineral strashimirite $\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4 \cdot 5\text{H}_2\text{O}$ is a hydrated hydroxyl divalent
39 copper arsenate [1, 2]. The mineral is of monoclinic symmetry with space group
40 $P2_1/m$ and may be compared with other hydroxyl copper arsenate minerals, including
41 euchroite $\text{Cu}_2(\text{AsO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$, olivenite $\text{Cu}_2(\text{AsO}_4)(\text{OH})$, cornwallite
42 $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$. Olivenite is monoclinic, space group $P2_1/n$ and is the most
43 common secondary mineral of the oxidized zone of hydrothermal deposits. Other
44 related copper and arsenate minerals are the minerals cornwallite $[\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4]$
45 and clinoclase $[\text{Cu}_3(\text{AsO}_4)(\text{OH})_3]$. Each of these minerals occurs in the oxidized
46 zones of copper deposits and olivenite is by far the commonest [3, 4]. Cornwallite and
47 clinoclase are rare secondary mineral that crystallise monoclinic, space group $P2_1/a$
48 [3, 5, 6].

49

50 The relative stabilities of the basic copper arsenates have been determined
51 using estimated chemical parameters and experimentally determined solubility
52 products [7, 8]. Magalhaes *et al.* have reported the relative stability of copper
53 arsenate minerals [9]. Normal anhydrous copper(II) arsenate is known as the
54 naturally occurring species lammerite $[\text{Cu}_3(\text{AsO}_4)_2]$, but it is very rare [10]. The more
55 basic stoichiometries occupy fields at higher pH as expected. Since olivenite is the
56 stable phase under chemical conditions intermediate to those that serve to stabilize
57 cornwallite and clinoclase, paragenetic relationships have been explored. [10]
58 Olivenite is often found with either cornwallite or clinoclase, but not together. The
59 stability of the basic copper arsenate minerals is related to their redox potential and
60 phase fields exist for the related minerals olivenite, cornubite $[\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4]$,
61 clinoclase and cornwallite. Thus, the structure of these phase related minerals are
62 related and should provide similar spectra, which should differ in terms of the
63 intensity and position of the bands according to the relative mole ratios of Cu/As/OH
64 and the number and site symmetry of the formula units in the unit cell of the minerals.

65

66 Whilst the infrared spectra of some minerals have been forthcoming, few
67 comprehensive studies of related minerals such as the basic copper arsenates have
68 been undertaken[11-13]. The structural investigation of some arsenates and the nature
69 of the hydrogen bond in these structures have been reported[14-24]. It was found that
70 the hydroxyl unit was coordinated directly to the metal ion and formed hydrogen
71 bonds to the arsenate anion[25]. The basic copper arsenates include a significant
72 number of diagenetically related minerals. Raman spectroscopy is important tool for
73 our understanding of diagenetically related minerals such as the basic copper arsenate
74 minerals. The aim of this paper is to interpret the Raman spectrum of strashimirite on
75 the basis of mineral structure, the structure of which is uncertain. This research
76 reported here, is part of systematic studies on the vibrational spectra of minerals of
77 secondary origin in the oxide supergene zone and their synthetic analogs.

78

79 **2. Experimental**

80

81 *2.1. Minerals*

82

83 The studied samples of the mineral strashimirite were found at the Zálesí
84 deposit, the Rychlebské hory Mountains, northern Moravia, Czech Republic, and
85 Svätodušná deposit near Lubietová, central Slovakia, Slovak Republic. These
86 strashimirite minerals are labelled sample A and sample B. These samples are
87 deposited in the mineralogical collections of the National Museum Prague. The
88 samples were analysed for phase purity by X-ray powder diffraction and no minor
89 significant impurities were found. Their refined unit-cell parameters for monoclinic
90 primitive space group are $a=9.56(1)$, $b=18.38(3)$, $c=9.10(1)$ Å, $\beta=97.26(9)^\circ$, $V=$
91 $1587(4)$ Å³ (CR) and $a=9.524(3)$, $b=18.536(6)$, $c=9.058(4)$ Å, $\beta=96.96(4)^\circ$,
92 $V=1587.1(9)$ Å³ (SR). Inferred values of unit-cell parameters are substantially
93 lower than those as yet published [26-28]. The refined parameters of strashimirite
94 are provided in Table 1. This phenomenon may be probably caused by observed
95 anionic isomorphism ($As \leftrightarrow P$, $As \leftrightarrow S$).

96 The minerals were analysed by electron microprobe (Cameca SX100, WD
97 mode) for chemical composition. The results (CR - mean of 6 point analysis) are CaO
98 0.51, FeO 0.06, CuO 50.31, CoO 0.30, NiO 0.54, ZnO 0.38, Al₂O₃ 0.06, Sb₂O₃ 0.08,
99 SiO₂ 0.09, As₂O₅ 37.20, P₂O₅ 0.04, SO₃ 0.55, H₂O_{calc.} 10.44, sum 100.57 wt. %
100 resulting to empirical formula (Cu_{7.59}Ca_{0.11}Ni_{0.09}Zn_{0.05}Co_{0.04}Al_{0.02}Fe_{0.01})_{Σ7.91}
101 [(AsO₄)_{3.89}(SO₄)_{0.08}(SiO₄)_{0.02}(PO₄)_{0.01}]_{Σ4.00}(OH)_{3.92} · 5H₂O. For SR sample (mean of 2
102 point analysis) are CaO 0.06, CuO 50.05, CoO 0.02, NiO 1.72, ZnO 0.22, Al₂O₃ 0.17,
103 Sb₂O₃ 0.02, SiO₂ 0.09, As₂O₅ 35.53, P₂O₅ 0.88, SO₃ 0.17, H₂O_{calc.} 10.46, sum 99.39
104 wt. % and empirical formula (Cu_{7.74}Ni_{0.28}Al_{0.04}Zn_{0.03}Ca_{0.01})_{Σ8.10}
105 [(AsO₄)_{3.80}(PO₄)_{0.15}(SO₄)_{0.02}(SiO₄)_{0.02}]_{Σ3.99}(OH)_{4.27} · 5H₂O. The basis of recalculating
106 is (As+Si+P+Sb) = 4 apfu; water contents were calculated on the basis of charge
107 balance and theoretical content of H₂O = 5 pfu. The chemical analysis of the two
108 strashimirite minerals are given in Table 2. The composition of this mineral has been
109 reported by Anthony *et al.* [29] (page 565).

110

111 The sample of cornubite from the Daly mine, Flinders Ranges, South Australia
112 was obtained from the collections of the Mineralogy Section, Museum Victoria,
113 Melbourne, Victoria, Australia (specimen M37793). Cornwallite and olivenite from
114 the Penberthy Croft mine, St Hilary, Cornwall, UK, were supplied by Mr John
115 Betterton. Samples of olivenite and clinoclase from the Tin Stope, Majuba Hill mine,
116 Utah, USA, were purchased from the Mineralogical Research Company. All were
117 checked for purity by powder X-ray diffraction and by SEM and microprobe methods.
118 Negligible amounts of phosphorus or transition metals other than copper were found
119 in the samples used for this spectroscopic study.

120

121 2.2. Raman spectroscopy

122

123 The crystals of strashimirite were placed on the stage of an Olympus BHSM
124 microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000
125 Raman microscope system, which also includes a monochromator, a filter system and
126 a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633
127 nm) at a resolution of 2 cm⁻¹ in the range between 100 and 4000

128 cm^{-1} . Repeated acquisition using the highest magnification was accumulated for 64
129 scans at 20 secs. to improve the signal to noise ratio. The instrument was calibrated
130 using the 520.7 cm^{-1} line of a silicon wafer.

131

132 *2.3 Infrared spectroscopy*

133 The FTIR spectrum of strashimirite was obtained with the FTIR Nicolet 740
134 spectrometer using the conventional KBr-disk technique. Infrared spectrum in the
135 range $4000\text{-}400 \text{ cm}^{-1}$ was obtained by the co-addition of 32 scans with a resolution of
136 2 cm^{-1} and a mirror velocity of 0.1496 cm/s . Spectral manipulation such as baseline
137 adjustment, smoothing and normalization were performed using the OMNIC software
138 package (Thermo Electron Corporation). Band component analysis was undertaken
139 using the same software package which enabled the type of fitting function to be
140 selected and allows specific parameters to be fixed or varied accordingly. Band fitting
141 was done using a Lorentz-Gauss cross-product function with the minimum number of
142 component bands used for the fitting process.

143

144

145 Spectral manipulation such as baseline adjustment, smoothing and
146 normalisation were performed using the Spectracalc software package GRAMS
147 (Galactic Industries Corporation, NH, USA). Band component analysis was
148 undertaken using the Jandel 'Peakfit' software package which enabled the type of
149 fitting function to be selected and allows specific parameters to be fixed or varied
150 accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with
151 the minimum number of component bands used for the fitting process. The Gauss-
152 Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken
153 until reproducible results were obtained ($r^2 > 0.995$).

154

155

156

157 **3. Results and discussion**

158

159 *3.1. Raman spectroscopy*

160

161 The Raman spectra of the tetrahedral anions in aqueous systems are well
162 known [30]. The Raman active symmetric stretching ν_1 vibration of the arsenate
163 anion is observed at 810 cm^{-1} and coincides with the position of the triply degenerate
164 Raman and infrared active antisymmetric stretching mode (ν_3). The doubly
165 degenerate Raman active symmetric bending mode (ν_2) is observed at 342 cm^{-1} and
166 the triply degenerate Raman and infrared active out-of-plane bending modes (ν_4) is
167 observed at 398 cm^{-1} . Of all the tetrahedral oxyanions spectra, the positions of the
168 arsenate vibrations occur at lower wavenumbers for naturally occurring mineral
169 oxyanions spectra [30]. Farmer lists a number of infrared spectra of arsenates
170 including the basic copper arsenates olivenite and euchroite[31]. Depending on the
171 symmetry of the anion, the bands may be infrared active but not Raman active, but
172 may be both. The effect of the arsenate ion in a crystal will be to remove the
173 degeneracy and allow splitting of the bands according to factor group analysis. The ν_1
174 and ν_3 bands of olivenite and euchroite were observed at $860, 828, 790\text{ cm}^{-1}$ and at
175 830 and 770 cm^{-1} respectively. The ν_4 (AsO_4^{3-}) bending modes were found at 493
176 and 452 cm^{-1} for olivenite and at 475 and 410 cm^{-1} for euchroite. No ν_2 bands were
177 registered. This is no doubt related to the fact the bands are found below 400 cm^{-1} .
178 Two OH stretching vibrations were observed in the infrared spectrum at 3580 and
179 3440 cm^{-1} for olivenite. The Raman and infrared spectra of strashimirite minerals A
180 and B are shown in Figures 1 and 2 respectively. The results of the Raman and
181 infrared spectra of strashimirite minerals together with the results of the Raman
182 spectra of olivenite, cornwallite, clinoclase and cornubite are reported in Table 3.

183

184

185 The Raman spectra of strashimirite from the two different deposits in the
186 region 700 to 1000 cm^{-1} are shown in Fig. 3. In the Raman spectrum of strashimirite
187 A, a broad intense band centred at 850 cm^{-1} is observed and may be band component
188 analysed into components at 831 and 852 cm^{-1} which are assigned to the ν_1 (AsO_4^{3-})
189 symmetric and ν_3 (AsO_4^{3-}) antisymmetric stretching modes. Low intensity bands are
190 also observed at 893 and 982 cm^{-1} . The latter is attributed to some phosphate
191 substitution, as is confirmed by X-ray diffraction and infrared spectroscopy. A
192 comparison may be therefore made with the infrared data of this mineral. In the

193 infrared spectrum of A (Fig. 4) intense infrared bands are observed at 760 and 833
194 cm^{-1} with two shoulder bands at 804 and 909 cm^{-1} . The latter band at 909 cm^{-1}
195 corresponds reasonably well with the Raman band at 893 cm^{-1} and the 833 cm^{-1}
196 infrared band corresponds to the Raman band at 839 cm^{-1} . Low intensity infrared
197 bands are observed at 1002, 1085 and 1123 cm^{-1} which are assigned to (PO_4^{3-}) for
198 (AsO_4^{3-}) substitution or to (SO_4^{2-}) substitution.

199

200 The Raman spectrum of strashimirite B in the 700 to 1000 cm^{-1} region shows
201 greater complexity. Bands are observed at 826, 843, 891 and 988 cm^{-1} . The band at
202 988 cm^{-1} may be probably attributed to the $\nu_1(\text{PO}_4^{3-})$ or $\nu_1(\text{SO}_4^{2-})$. A band is also
203 observed at 771 cm^{-1} . The attribution of which is unknown. One possibility is that
204 this is a water librational mode. Such a band should show greater intensity in the
205 infrared spectrum but this is not the case. The two bands at 826 and 843 cm^{-1} are
206 assigned to the $\nu_1(\text{AsO}_4^{3-})$ symmetric and $\nu_3(\text{AsO}_4^{3-})$ antisymmetric stretching
207 modes. The infrared spectrum of strashimirite B is reported in Fig. 1b (supplementary
208 information). An intense infrared band is found at 843 cm^{-1} with two shoulder bands
209 at 826 and 891 cm^{-1} . The correspondence between the infrared data and Raman data
210 is good for strashimirite B. Because of the diagenetic relationship between the basic
211 copper arsenate minerals, a comparison of the Raman spectra with the other minerals
212 can be made (see Table 3). The Raman spectrum of olivenite shows two (AsO_4^{3-})
213 bands at 853 and 820 cm^{-1} ; cornwallite at 859 and 806 cm^{-1} , cornubite at 815 and 780
214 cm^{-1} and clinoclase at 823 and 771 cm^{-1} [30, 32]. Additional very weak Raman bands
215 for olivenite are observed at 880 and 790 cm^{-1} . The most intense band is assigned to
216 the ν_1 symmetric stretching vibration. This assignment differs from that described by
217 Sumin de Portilla [25]. In his work, the ν_3 mode was described as splitting into four
218 components at 870, 830, 800 and 750 cm^{-1} . Farmer suggested that the ν_1 and ν_3
219 modes overlapped and were to be found at the same frequency [31]. Whilst this is
220 highly unusual, it is suggested that the two vibrations at 853 and 820 cm^{-1} are the
221 (AsO_4^{3-}) symmetric and antisymmetric stretching vibrations, respectively. Griffith
222 reported the Raman spectrum of olivenite[33] at 880 (A^1), 856 (B_{2u}), 810 (A^1) and 790
223 (B_{2u}) cm^{-1} . The observation of the bands 853 and 820 cm^{-1} is in good agreement with
224 the data published by Griffith [33]. The most intense bands in the Raman spectra are
225 the bands at 853 and 810 cm^{-1} . Factor group analysis suggests that there should be

226 one active Raman band and one active infrared band in the (AsO_4^{3-}) stretching region.
227 Additional bands result from a loss of site symmetry. The difference in intensity is
228 related to the number of (AsO_4^{3-}) units involved in this site symmetry reduction. Thus
229 the other two infrared bands observed at 800 and 750 cm^{-1} for olivenite are the
230 corresponding ν_3 vibrations. The second band observed at 806 and 771 cm^{-1} is more
231 intense for cornwallite and clinoclase. The (AsO_4^{3-}) stretching vibration for olivenite
232 and cornwallite are in similar band positions, suggesting a similar molecular structure.
233 For cornubite two bands are observed at 815 and 780
234 cm^{-1} .

235
236 Stoilova and Minceva-Stefanova reported the infrared spectrum of a type
237 strashimirite mineral from Bulgaria[1]. These researchers identified infrared bands at
238 766 and 863 cm^{-1} and assigned these bands to the ν_1 (AsO_4^{3-}) symmetric and ν_3
239 antisymmetric stretching modes. The intense Raman bands at 845 cm^{-1} for
240 strashimirite A and 843 cm^{-1} for strashimirite B tend to suggest that the assignation of
241 Stoilova and Minceva-Stefanova may compliment the Raman and infrared results
242 reported in this work. . Further the bands are highly polarised, confirming the
243 assignment of the Raman band. Magalhaes *et al.* studied the solution chemistry of
244 copper arsenate mineral [9]. These authors reported the relationship between
245 euchroite $\text{Cu}_2(\text{AsO}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$, strashimirite $\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4\cdot 4\text{H}_2\text{O}$ and arhbarite
246 $\text{Cu}_2\text{Mg}(\text{AsO}_4)(\text{OH})_3$. Complex paragenetic relationships exist between these copper
247 arsenate minerals. An example of this relationship exists for the minerals of the
248 Zapachitsa deposit in Bulgaria. The sequence of deposition of the copper arsenate
249 minerals is proposed to be cornwallite-olivenite-tyrolite-strashimirite-conichalcite. It
250 is possible that the mineral sample reported based upon infrared spectra, by Stoilova
251 and Minceva-Stefanova may be likely a mixture of some minerals from this mineral
252 paragenetic sequence.

253
254 The Raman spectra of strashimirite A and B in the 100 to 600 cm^{-1} region are
255 shown in Fig. 5. A broad band centred upon 500 cm^{-1} for strashimirite A, which may
256 be resolved into component bands at 467, 497, 526 and 554 cm^{-1} probably includes
257 bands attributable to the ν_4 (AsO_4^{3-}) bending mode. The observation of multiple
258 bands suggests that the symmetry of the (AsO_4^{3-}) ion has been reduced. The shoulder
259 band at 467 cm^{-1} is probably ascribed to the CuO stretching mode. The higher

260 wavenumber band may be assigned to a water librational mode. A band in this
261 position is expected although in the Raman spectrum may be of low intensity. A
262 Raman band is observed at 560 cm^{-1} for strashimirite B. The band at 507 cm^{-1} for
263 strashimirite B is broad and is assigned to the $\nu_4(\text{AsO}_4)^{3-}$ bending mode. Stoilova and
264 Minceva-Stefanova reported infrared bands at 430, 470 and 92 and assigned these
265 bands to $\nu_4(\text{AsO}_4^{3-})$ bending mode [1]. The appearance of multiple bands in the ν_4
266 (AsO_4^{3-}) bending region further provides evidence for the reduction of the symmetry
267 of the (AsO_4^{3-}) anion to C_{2v} or even lower.

268

269 The low wavenumber region of the basic copper arsenates is complex and it is
270 difficult to separate the Raman bands according to their symmetry. The spectrum of
271 the low wavenumber region of the basic copper arsenates may be divided into three
272 separate regions: (a) 450 to 650 cm^{-1} (b) 400 to 450 cm^{-1} and (c) 400 to 250 cm^{-1} . It is
273 proposed that these three regions define the (a) ν_4 modes (b) ν_2 modes and (c) (AsO_4^3)
274 lattice modes. The ν_2 bending vibration should be common to all the basic copper
275 arsenates spectra and should be intense. The (AsO_4^{3-}) bending mode (ν_2) should be
276 found at around 342 cm^{-1} . In the Raman spectrum of A, two bands at 337 and 393
277 cm^{-1} may be ascribed to this vibrational mode. Three Raman bands are observed for
278 B at 343 , 374 and 411 cm^{-1} . The first band is attributed to the $\nu_2(\text{AsO}_4^{3-})$ bending
279 mode. The band at 350 cm^{-1} for olivenite, 340 cm^{-1} for cornwallite and at 380 cm^{-1} is
280 assigned to the $\nu_2(\text{AsO}_4^{3-})$ symmetric bending vibration. The observation of this
281 mode below 400 cm^{-1} has been predicted but not reported [31]. Our results differ
282 from those of Griffith who reported bands at 324 and 310 cm^{-1} for the (AsO_4^{3-})
283 bending modes of olivenite [33].

284

285 In the low wavenumber region of the basic copper arsenates, intense Raman
286 bands are observed (Fig. 5). In the Raman spectrum of the low wavenumber region
287 for A, Raman bands are observed at 152 , 172 , 220 , 239 and 294 cm^{-1} . In the Raman
288 spectrum of the low wavenumber region bands for B are observed at 144 , 183 , 219 ,
289 242 and 299 cm^{-1} . The intense sharp band at 299 cm^{-1} is assigned to the AsO
290 stretching vibration. In the structure of strashimirite it is proposed (without the single
291 crystal X-ray evidence) that the (AsO_4^3) units are not equivalent and thus more than
292 one CuO vibration will exist. Stoilova and Minceva-Stefanova tabled results for the
293 CuO stretching vibration at 492 and 540 cm^{-1} in the infrared spectrum [1]. For

294 olivenite intense bands are observed at 310 and 286 cm^{-1} and are assigned to the CuO
295 stretching vibration. A second low intensity band is observed at 258 cm^{-1} and may be
296 also assigned to a CuO stretching vibration. Two CuO vibrations exist because there
297 are two types of units namely OH and AsO_4 units coordinating to the copper. The
298 intense bands for A at 144 and 183 cm^{-1} may be assigned to OCuO bending
299 vibrations. Intense Raman bands are also observed at 219 and 151 cm^{-1} for olivenite,
300 198 and 172 cm^{-1} for cornwallite and at 189 and 185 cm^{-1} for clinoclase. These bands
301 may also be assigned to OCuO bending vibrations.

302

303 The Raman spectrum in the OH stretching region of strashimirite A and B are
304 shown in Fig. 6. The infrared spectra of the strashimirite minerals are shown in Fig.
305 7. The Raman spectrum of A shows three resolved bands at 3450, 3588 and 3585 cm^{-1} .
306 The first two bands are attributed to water stretching vibrations and the band at
307 3585 cm^{-1} to the OH stretching vibrations of the hydroxyl units. The infrared
308 spectrum of A shows a complex set of overlapping bands. Band component analysis
309 resolves component bands at 2728, 3012, 3235 cm^{-1} ascribed to water stretching
310 bands; and component bands at 3361 and 3514 cm^{-1} attributed to the OH stretching
311 vibrations of hydroxyl ions. The Raman spectrum in this spectral region for B shows
312 a broad band centred on 3444 cm^{-1} with a sharp intense band at 3497 cm^{-1} . One likely
313 assignment is that the first band is due to the water stretching vibration and the latter
314 to the stretching vibration of the hydroxyl units. As for strashimirite A, a complex set
315 of overlapping infrared bands are observed. Infrared bands are observed at 2731,
316 3059 and 3273 cm^{-1} assigned to water stretching bands and at 3439 and 3579 cm^{-1}
317 assigned to the OH unit stretching vibrations of the hydroxyl ions.

318

319 Stoilova and Minceva-Stefanova reported the infrared OH stretching bands at
320 3380, 3420 and 3500 cm^{-1} [1]. These values differ from those reported in Fig. 5.
321 These authors considered that these bands provided evidence of strong hydrogen
322 bonds in the strashimirite mineral. Low intensity infrared bands found by these
323 authors were observed at 2133, 2740 and 2900 cm^{-1} and provided further evidence of
324 strong hydrogen bonds in the strashimirite structure. In our Raman spectrum of
325 strashimirite low intensity bands were found at 2124, 2346, 2924 and 3058 cm^{-1} . In
326 our infrared spectrum, bands were observed at around 2730 and 2842 cm^{-1} supporting
327 the proposition by Minceva-Stefanova for strong hydrogen bonding in the

328 strashimirite structure. The observation of these bands in our Raman and infrared
329 spectra supports the concept of strong hydrogen bond interactions between the water
330 units and the arsenate anions.

331

332 A comparison may be made with the Raman spectrum of the hydroxyl
333 stretching region of other basic copper arsenates (Table 3). The Raman spectrum of
334 olivenite displays two overlapping bands centred upon 3464 and 3437 cm^{-1} ; and for
335 cornwallite two partially band-separated peaks are observed at 3411 and 3350 cm^{-1} .
336 In the Raman spectrum of cornubite, two bands are observed at 3324 and 3042 cm^{-1} .
337 For clinoclase two well separated bands separated peaks are observed at 3559 and
338 3339 cm^{-1} . The observation of two hydroxyl-stretching vibrations means that there
339 are two distinct and different hydroxyl units in the basic copper arsenate minerals.
340 The difference between the peak positions of olivenite and cornwallite is related to the
341 strength of the hydrogen bond formed between the hydroxyl unit and adjacent
342 arsenate units. This bonding is much stronger in cornwallite as indicated by the lower
343 wavenumber position of the hydroxyl-stretching vibrations. One interpretation is that
344 the higher wavenumber vibration is ascribed to the As-OH vibration and the lower
345 wavenumber hydroxyl stretching frequency to the As-OH \cdots O vibration.

346

347 The infrared spectra of the strashimirite minerals A and B are shown in Fig. 8.
348 The 1300 to 1800 cm^{-1} spectral profile for A, may be resolved into component bands
349 at 1617, 1649 and 1673 cm^{-1} with additional low intensity bands at 1420 and 1459
350 cm^{-1} . These latter two bands may indicate the presence of carbonate anions.
351 However, no carbonate ions were inferred from the analysis. It is likely these low
352 intensity infrared bands are due to overtone or combination bands. The infrared band
353 at 1617 cm^{-1} is typical of weakly hydrogen bonded water and the two bands at 1649
354 and 1673 cm^{-1} are attributed to strongly hydrogen bonded water. The identification of
355 these bands supports the concept that water is strongly bonded in the structure of
356 strashimirite and is required for the stability of the mineral. The infrared spectrum of
357 strashimirite B also shows bands at 1624 and 1674 cm^{-1} , which supports the concept
358 of two types of water in the strashimirite structure.

359

360

361 *3.2. Diagenetic relationships between the basic copper arsenate minerals*

362

363 Williams [10] has presented phase stability relationships between a range of
364 diagenetically related minerals including the basic copper arsenates. Magalhaes et al.
365 [34] reported the relative stabilities of the basic copper arsenates using estimated
366 chemical parameters and experimentally determined solubility products are available
367 [7, 8]. The difference in stability is attributed to pH, temperature of crystallization and
368 the relative redox potentials. One possible set of relationships is as follows:

369 Euchroite $\text{Cu}_2(\text{AsO}_4)(\text{OH})\cdot 3\text{H}_2\text{O} \rightarrow$ olivenite $\text{Cu}_2(\text{AsO}_4)(\text{OH})$

370 \rightarrow strashimirite $\text{Cu}_8(\text{AsO}_4)_4(\text{OH})_4\cdot 5\text{H}_2\text{O} \rightarrow$ arhbarite $\text{Cu}_2\text{Mg}(\text{AsO}_4)(\text{OH})_3$. A

371 complex set of equilibria exists between these minerals. The presence of other cations
372 in the solution such as Ca^{2+} can affect these equilibria [34].

373

374 **4. Conclusions**

375

376 Raman spectroscopy has been used to characterise the mineral strashimirite.
377 Two samples from the Czech and Slovak Republics were used. The Raman spectra of
378 the two minerals differed and this difference may probably be connected with anionic
379 isomorphic substitution $\text{As} \Leftrightarrow \text{S}$ for A and $\text{As} \Leftrightarrow \text{P}, \text{S}$ for B. Characteristic Raman
380 bands of the $(\text{AsO}_4)^{3-}$ stretching and bending vibrations were identified and described.
381 Raman bands attributable to the OH stretching vibrations of water and hydroxyl units
382 were analysed.

383

384 A comparison was made with the Raman spectrum of strashimirite with other selected
385 basic copper arsenate minerals. A description of the relative stability of the mineral
386 strashimirite relative to other basic copper arsenate minerals is provided.

387

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389

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395

396

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- 458
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- 460

461 **Table 1**

462 **Refined unit-cell parameters for strashimirite**

Occurrence	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$\beta/^\circ$	Volume/ Å^3
Zálesí (CR)	9.56(1)	18.38(3)	9.10(1)	97.26(9) ^o	1587(4)
Lubietová (SR)	9.524(3)	18.536(6)	9.058(4)	96.96(4)	1587.1(9)
Zapačica [35]	9.70	18.90	9.127	97.25	1660
Novoveská Huta [28, 36]	9.708(6)	18.84(9)	8.936(7)	97.22(5)	1621.4
Redziny [37]	9.719(2)	18.806(5)	8.937(3)	97.31(3)	1620.2

463

464

465 **Table 2**

466 **Chemical composition of strashimirite (wt. %)**

	Lubietová (SR) ^a		Zálesí (CR) ^b			Ideal ^c
	mean	range	mean	range		
CaO	0.06	0.04 - 0.07	0.51	0.38	- 0.65	0.00
FeO	0.00	0.00 - 0.00	0.06	0.00	- 0.13	0.00
CuO	50.05	50.03 - 50.08	50.31	47.80	- 52.57	52.07
CoO	0.02	0.02 - 0.02	0.30	0.26	- 0.38	0.00
NiO	1.72	1.72 - 1.73	0.54	0.42	- 0.69	0.00
ZnO	0.22	0.16 - 0.27	0.38	0.31	- 0.43	0.00
Al ₂ O ₃	0.17	0.16 - 0.19	0.06	0.00	- 0.12	0.00
Sb ₂ O ₃	0.02	0.02 - 0.03	0.08	0.05	- 0.11	0.00
SiO ₂	0.09	0.07 - 0.11	0.09	0.03	- 0.21	0.00
As ₂ O ₅	35.53	35.27 - 35.80	37.20	36.22	- 38.26	37.61
P ₂ O ₅	0.88	0.86 - 0.90	0.04	0.02	- 0.05	0.00
SO ₃	0.17	0.17 - 0.18	0.55	0.45	- 0.64	0.00
H ₂ O*	10.46	0.00 - 0.00	10.44			10.32
total	99.39		100.57			100.00

467 ^a mean and range of two point analyses

468 ^b mean and range of six point analyses

469 ^c composition for ideal formula Cu₈(AsO₄)₄(OH)₄·5H₂O

470 H₂O* - content calculated on the basis of charge balance and theoretical content 5

471 H₂O.

472

Sample A	Sample A	Sample B	Sample B	Olivenite	Cornwallite	Clinoclase	Cornubite
Raman /cm ⁻¹	Infrared /cm ⁻¹	Raman /cm ⁻¹	Infrared /cm ⁻¹	Raman /cm ⁻¹	Raman /cm ⁻¹	Raman /cm ⁻¹	Raman /cm ⁻¹
3585	3514		3579			3559	3324
	3361			3464	3411		
3488		3497					
3450		3444	3439	3437			
	3215		3273		3350	3339	
	3012		3059				3042
	2842		2859				
	2728		2731				
	1649		1650				
	1617		1624				
	1459		1579				
	1420		1505				
	1123						
	1085				1087		1051
		988	988		962	983	962
	909	891	891	857	877	850	
852	833	843	843	853	859	832	815
831	804	826	826	819	806		
	760				763	783	780
	710	712	712	632	603	607	
554		560		590			
526		507		554	536	539	525
497		496		496	509	508	496
467		411		421	416	438	440
393		374		360	363		398
337	343			346	347	348	365
294	299			335	330	318	327

473

474 **Table 3 Results of the vibrational spectroscopic analysis of strashimirite and in**
475 **comparison with the Raman spectra of other basic copper arsenates**

476

477 **Legends to figures**

478

479 Fig. 1 Raman spectrum of strashimirite samples A and B in the 100 to 4000 cm^{-1}
480 region.

481 Fig. 2 Infrared spectrum of strashimirite samples A and B in the 600 to 4000 cm^{-1}
482 region.

483 Fig. 3 Raman spectrum of strashimirite samples A and B in the 700 to 1000 cm^{-1}
484 region.

485 Fig. 4 Infrared spectra of strashimirite samples A and B in the 700 to 1300 cm^{-1}
486 region.

487

488 Fig. 5 Raman spectrum of strashimirite samples A and B in the 100 to 600 cm^{-1}
489 region.

490 Fig. 6 Raman spectrum of strashimirite samples A and B in the OH stretching
491 region.

492 Fig. 7 Infrared spectrum of strashimirite samples A and B in the OH stretching
493 region.

494 Fig. 8 Infrared spectrum of strashimirite samples A and B in the 1300-1800 cm^{-1}
495 stretching region.

496

497

498 **Legends to tables**

499

500 Table 1 Refined unit-cell parameters for strashimirite

501 Table 2 Chemical composition of strashimirite (wt. %)

502 Table 3 Results of the vibrational spectroscopic analysis of strashimirite

503