Raman microscopy of the mixite mineral $BiCu_6(AsO_4)_3(OH)_6{\cdot}3H_2O$ from the Czech Republic.

Ray L. Frost, [1] • Jiří Čejka, [1,2] Jiří Sejkora [2] Jakub Plášil, [2] Silmarilly Bahfenne, [1] and Sara J. Palmer [1]

[1] Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[2] National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

ABSTRACT:

Raman microscopy of the mixite mineral $BiCu_6(AsO_4)_3(OH)_6{\cdot}3H_2O$ from Jáchymov and from Smrkovec (both Czech Republic) has been used to study their molecular structure, which is interpreted and the presence of $(AsO_4)^{3-}$, $(AsO_3OH)^{2-}$, $(PO_4)^{3-}$ and $(PO_3OH)^{2-}$ units, molecular water and hydroxyl ions were inferred. O-H…O hydrogen bond lengths were calculated from the Raman and infrared spectra using Libowitzky's empirical relation. Small differences in the Raman spectra between both samples were observed and attributed to compositional and hydrogen bonding network differences.

KEYWORDS: mixite, arsenate, hydrogen arsenate, phosphate, hydrogen phosphate Raman, infrared, spectroscopy, molecular water, hydroxyl ions, hydrogen bonds, O-H…O hydrogen bond lengths

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

INTRODUCTION

Minerals of the mixite group have the general formula $MCu_6(TO_4)_3(OH)_6 \cdot 3\ H_2O$. Cations such as Ca^{2+}, Pb^{2+}, Al^{3+}, Bi^{3+}, Y^{3+} and other REE^{3+} are found to occupy the octahedrally coordinated M site; only As and P have been found in significant amounts at the T tetrahedral site. Minerals of this group have been classified on the basis of the occupancy of the M and T sites: mixite [Bi; As], agardite-(Y) [Y; As], goudeyite [Al; As], petersite-(Y) [Y; P], zálesíite [Ca; As], agardite-(La) [La; As], agardite-(Ce) [Ce; As], plumboagardite [Pb, As] and calciopetersite [Ca, P] [1-4]. The names agardite-(Nd), agardite-(Dy) and petersite-(Nd) were ocassionaly used [2,5] but these minerals have not been approved by the IMA [4]. Large extent of isomorphy in the proportion of the major cations and tetrahedral site (As⇔P), too, is well documented on the natural members of this group [6-8]. Substitution of a trivalent cation (Bi^{3+}, Y^{3+}, REE^{3+}) at the M site by divalent ones (Ca^{2+}, Pb^{2+}) is charge balanced by concominant substitution of OH^- for O^{2-} at the O(3) site in the crystal structure (attributed to AsO_3OH group) [1,3,4,9]. The crystal structure of natural members of mixite group reveal microporous framework [9-10] and some H_2O groups may well have a zeolitic character [8,11-13].

Mixite, hydrated copper bismuth arsenate, with ideal formula $BiCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$ was first found in 1880 on the Geister vein at Jáchymov (Czech Republic) by mine engineer Anton Mixa [14]. It crystallizes in the hexagonal space group $P6_3/m$ [10] and typically occurs as green radiating acicular prisms and fibrous encrustations. Mixite, similarly as other minerals of the mixite group, occurs as a supergene mineral in the oxide zone of ore occurrences and deposits in close association with bismutoferrite, bismutite, walpurgite and other supergene minerals.

Infrared and Raman spectra of some minerals of the mixite group and their synthetic analogues (mixite [15,16], agardite [17,18] , goudeyite [19]) have been studied. From the published Raman and infrared spectra, it was inferred that in the structure of these compounds may be present beside of $(AsO_4)^{3-}$ also $(HAsO_4)^{2-}$ and $(H_2AsO_4)^-$ ions because of necessary charge balance. However, any presence of the $(H_2AsO_4)^-$ ion in such structures is very doubtful and does not agree with the structure analysis.

This paper is a part of a vibrational spectroscopic investigation on supergene minerals originating in oxidation zone [20-24]. The aim of this paper is to characterise mixite samples

from two Czech occurrences (Jáchymov, Smrkovec) using Raman and infrared spectroscopy, and to compare the results with their chemical composition. Recently, Raman spectroscopy has proved to be a most useful tool for the study of molecular structure of minerals containing oxyanions [25-27].

EXPERIMENTAL

Minerals

The studied samples of the mineral mixite were found at the Smrkovec ore occurrence, the Slavkovský les Mountains, western Bohemia, Czech Republic [28], and at the Rovnost deposit, the Jáchymov ore district, the Krušné hory Mountains, Northern Bohemia, Czech Republic. The samples were analysed for phase purity by X-ray powder diffraction and no minor significant impurities were found. Their refined unit-cell parameters for hexagonal space group $P6_3/m$ a=13.637(1), c=5.910(1) Å, V= 951.8(2) Å^3 (Smrkovec), and a=13.620(1), c=5.903(1) Å, V=948.2(2) Å^3 (Jáchymov), are comparable with the data published for this mineral phase [10,29].

The mineral samples were analysed by electron microprobe (Cameca SX100, WD mode) for chemical composition. The results (Smrkovec - mean of 3 point analysis) are CaO 0.85, FeO 0.11, PbO 3.06, CuO 41.76, Al_2O_3 0.03, Bi_2O_3 16.24, SiO_2 0.83, As_2O_5 26.65, P_2O_5 1.87, H_2O (10.12), sum 102.13 wt. %, and empirical formula: $(Bi_{0.77}Ca_{0.17}Pb_{0.15}Fe_{0.11})_{\Sigma 1.20}Cu_{5.79}[(AsO_4)_{2.17}(AsO_3OH)_{0.39}(PO_4)_{0.29}(SiO_4)_{0.15}]_{\Sigma 3.00}(OH)_{6.00} \cdot 3H_2O$; Jáchymov (mean of 3 point analyses): CaO 0.50, FeO 0.14, PbO 2.77, Cu 44.22, Al_2O_3 0.14, Bi_2O_3 16.16, SiO_2 1.04, As_2O_5 26.32, P_2O_5 1.99, H_2O (10.01), sum 103.29 wt. % resulting to empirical formula $(Bi_{0.76}Pb_{0.14}Ca_{0.10}Al_{0.03}Fe_{0.02})_{\Sigma 1.05}Cu_{6.08}[(AsO_4)_{2.34}(AsO_3OH)_{0.16}(PO_4)_{0.31}(SiO_4)_{0.19}]_{\Sigma 3.00}(OH)_{6.00} \cdot 3H_2O$. The basis of recalculating is (P+As+Si) = 3.00 apfu; water contents were calculated on the basis of theoretical content H_2O = 3 pfu and charge balance.

Raman spectroscopy

The crystals of mixite were placed and oriented on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x and 50x objectives. The

microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a notch filter system and a CCD detector. The Raman spectra were excited by a He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The laser power was measured as 0.1 watts. Previous studies by the authors provide more details of the experimental technique. Further details have been published [30-33].

Infrared spectroscopy

Infrared spectra of both mixite samples were recorded by micro diffuse reflectance method (DRIFTS) on a Nicolet Magna 760 FTIR spectrometer (range 4000-600 cm^{-1}, resolution 4 cm^{-1}, 128 scans, 2 level zero-filtering, Happ-Genzel apodization), equipped with Spectra Tech InspectIR micro FTIR accessory. Each sample of amount less than 0.050 mg was mixed without using pressure with KBr. Samples were immediately recorded together with the same KBr as a reference.

Band component analyses for both Raman and infrared spectra were undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz- Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz- Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of R^2 greater than 0.995.

RESULTS AND DISCUSSION

According to Myneni *et al.* [38,39] and Nakamoto [40], $(AsO_4)^{3-}$ is a tetrahedral unit, which exhibits four fundamental vibrations: the ν_1 symmetric stretching vibration (A_1) 818 cm^{-1} , Raman active; the doubly degenerate ν_2 symmetric bending vibration (E) 350 cm^{-1}, Raman active; the triply degenerate ν_3 antisymmetric stretching vibration (F_2) 786 cm^{-1}, and the

triply degenerate ν_4 bending vibration (F_2) 405 cm^{-1} , both infrared and Raman active. Protonation, metal complexation, and/or adsorption on a mineral surface should cause change in $(AsO_4)^{3-}$ symmetry from T_d to lower symmetries, such as C_{3v}, C_{2v}, C_1. This is connected with the splitting of degenerate vibrations of $(AsO_4)^{3-}$ and the shifting of the As-OH stretching vibrations to different wavenumbers. Such chemical interactions reduce $(AsO_4)^{3-}$ tetrahedral symmetry, as mentioned above, to either C_{3v}/C_3 (corner-sharing), C_{2v}/C_2 (edge-sharing, bidentate binuclear), or C_1/C_s (corner-sharing, edge-sharing, bidentate binuclear, multidentate) [38,39]. In association with $(AsO_4)^{3-}$ symmetry and coordination changes, the A_1 band may shift to different wavenumbers and the doubly degenerate E and triply degenerate F modes may give rise to several new A_1, B_1, and/or E vibrations [38,39]. In the absence of symmetry deviations, $(AsO_3OH)^{2-}$ in C_{3v} symmetry exhibit the ν_s As-OH and ν_{as} and ν_s As-O_3 vibrations together with corresponding the δ As-OH in-plane bending vibration, δ As-OH out-of-plane bending vibration, ν_s As-O_3 stretching vibration and δ_{as} As-O_3 bending vibration [36,37,41]. Keller [41] assigned observed the following infrared bands in $Na_2(AsO_3OH)\cdot 7H_2O$ 450 and 360 cm^{-1} to the δ_{as} (ν_4) AsO_3 bend (E), 580 cm^{-1} to the δ As-OH out-of-plane bend, 715 cm^{-1} to the ν As-OH stretch (A_1), 830 cm^{-1} to the ν_{as} AsO_3 stretch (E), and 1165 cm^{-1} to the δ As-OH in plane bend. In the Raman spectrum of $Na_2(AsO_3OH)\cdot 7H_2O$, Vansant *et al.* [36] attributed observed Raman bands to the following vibrations 55, 94, 116 and 155 cm^{-1} to lattice modes, 210 cm^{-1} to ν (OH…O) stretch, 315 cm^{-1} to AsO_3 rocking, 338 cm_{-1} to the δ_s AsO_3 bend, 381 cm^{-1} to the δ_{as} AsO_3 bend, 737 cm^{-1} to the ν_s As-OH stretch (A_1), 866 cm^{-1} to the ν_{as} stretch (E). Because of relatively high content of P^{5+} (~0.3 apfu), also bands related to the $(PO_4)^{3-}$ and $(PO_3OH)^{2-}$ vibrations are expected to be observed in the Raman and infrared spectra ($(PO_4)^{3-}$: δ_s (ν_2) 410-490 cm^{-1}, δ_{as} (ν_4) 510-670 cm^{-1}, ν_1 930-990 cm^{-1}, ν_3 975-1140 cm^{-1}; $(PO_3OH)^{2-}$: δ (O_3PO) 350-580 cm^{-1}, γ POH 700-900 cm^{-1}, ν POH 860-915 cm^{-1}, ν_s PO_3 940-1010 cm^{-1}, ν_{as} 1040-1170 cm^{-1}, δ POH 1210-1400 cm^{-1}, and combination bands at 1400-1750 cm^{-1}), if they are Raman and/or infrared active [42].

Mixite is the mineral with a general formula $BiCu_6(AsO_4)_3(OH)_6\cdot 3H_2O$ and as such will have three different vibrating units which will contribute to the overall spectral profile: (a) namely the OH units (b) the water molecules and (c) the arsenate $(AsO_4)^{3-}$ groups – a part of them, however, may be substituted by $(AsO_3OH)^{2-}$ groups because of necessary charge balance. The first two vibrating species will contribute to the high wavenumber region whilst the $(AsO_4)^{3-}$ and $(AsO_3OH)^{2-}$ units will show Raman bands below 1000 cm^{-1} [34]. Vibrational

spectroscopy has been used to study the coordination chemistry of $(AsO_4)^{3-}$ ions for some considerable time [34-39]. Vibrational spectroscopic studies have shown that the symmetry of the $(AsO_4)^{3-}$ polyhedron are strongly distorted and the $(AsO_4)^{3-}$ vibrations are strongly influenced by protonation, cation presence and water coordination [36-39]. Of all the tetrahedral oxyanions, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions. There are one symmetrically distinct M^{3+}/M^{2+} (Bi^{3+}/Ca^{2+}), one symmetrically distinct Cu^{2+}, and one symmetrically distinct As^{5+} in the crystal structure of mixite [10]. Respecting the existence of only one As site and a disorder character of substitution $(OH)^- \Leftrightarrow O^{2-}$ at one oxygen position, mixite may be formulated as $(M^{3+}, M^{2+})Cu_6[(As,P)O_3(O,OH)]\cdot 3H_2O$. No substantial differences in unit cell parameters are between the studied mixite samples. Mixite from Jáchymov slightly differs from the mixite from Smrkovec in the content of P^{5+} (0.31/0.29 apfu), Si^{4+} (0.19/0.15 apfu), and significantly in calculated $(AsO_3OH)^{2-}$ content (0.16/0.39 apfu).

The stretching vibrations of $[(As,P)O_3(O,OH)]$ units in mixite from Smrkovec and Jáchymov in the 700 to 1200 cm^{-1} region of the Raman spectra are shown in Fig. 1. The infrared spectra of both mineral samples are given in Fig. 2. The spectra of the two mixite samples are very similar as expected. An intense Raman band is observed at ~850 cm^{-1} for mixite. This band is assigned to the ν_1 $(AsO_4)^{3-}$ symmetric stretching vibration. It corresponds to an infrared band at 848 cm^{-1} (S) and 844 cm^{-1} (J). Raman and infrared bands of the ν (AsO_3) symmetric and antisymmetric stretching vibrations may overlap the ν_1 $(AsO_4)^{3-}$ band. Other Raman bands (855 and 805 cm^{-1} (S), 881, 837 and 806 cm^{-1} (J)) and infrared bands (814 and 797 cm^{-1} (S) and 807 and 799 cm^{-1} (J) are assigned to the split ν_3 $(AsO_4)^{3-}$ antisymmetric stretching vibrations, ν_{as} (AsO_3) stretching vibrations and those close to 725 and 700 cm^{-1} to the ν As-OH stretching vibrations of the $(AsO_3OH)^{2-}$ units. Raman bands at 955 cm^{-1} (S) and 991 cm^{-1} (J) and infrared bands at 1012 and 970 cm^{-1} (S) and 1173, 1110, 1089, 1057 and 997 cm^{-1} (J) are attributed to the ν_3 and ν_1 $(PO_4)^{3-}$ stretching vibrations. Some of these bands, however, may be connected with the δ As-OH in-plane bending vibrations and δ P-OH in-plane bending vibrations and ν_{as} (PO_3) stretching vibrations of $(AsO_3OH)^{2-}$ and $(PO_3OH)^{2-}$ units [36-39,41,42]. Infrared bands at 657 cm^{-1} (S) and 607 cm^{-1} (J) may be probably related to the libration mode of water molecules.

A number of Raman bands are observed in the 350 to 550 cm^{-1} region (Fig. 3). Bands at 553, 529 and 494 cm^{-1} (S) and 554, 531 and 500 cm^{-1} (J) are assigned to the δ_{as} (ν_4) triply degenerate $(PO_4)^{3-}$ bending vibrations, δ_{as} doubly degenerate (PO_3) bending vibration, and δAs-OH out-of-plane bending vibration [41]. Bands at 472 and 460 cm^{-1} (S) and 472 and 421 cm^{-1} (J) may be assigned to the δ_{as} (ν_4) triply degenerated $(AsO_4)^{3-}$ bending vibration, δ_{as} (AsO_3) bending vibration and δ_{as} (ν_2) $(AsO_4)^{3-}$ doubly degenerate bending vibration. Bands at 390 and 311 cm^{-1} (S) and 390 and 317 cm^{-1} (J) are assigned to the δ_s (ν_2) doubly degenerate $(AsO_4)^{3-}$ bending vibration and δ doubly degenerate (AsO_3) bending vibration [36,37,41]. Raman bands in the region from 284 to 105 cm^{-1} (S) and 282 to 106 cm^{-1} (J) may be related to cation-oxygen vibrations and lattice vibrations.

The Raman spectra of the ν OH stretching region are shown in Fig. 4 and the infrared spectra are given in Fig. 5. Sharp Raman bands at 3470 cm^{-1} (S) and 3451 cm^{-1} (J) together with sharp infrared bands at 3483 cm^{-1} (S) and 3483 cm^{-1} (J) are assigned to the weakly hydrogen bonded hydroxyl ions. Corresponding O-H…O hydrogen bond lengths are (Å/cm^{-1}) 2.87/3470 and 2.88/3483(S) and 2.85/3451 and 2.88/3483 (J) [43]. Such hydrogen bonds may be understood as weak, because they are over 2.70 Å [43-45]. Raman bands at 3361 cm^{-1} (S) and 3392 cm^{-1} (J) and infrared bands at 3381 and 3243 cm^{-1} (S) and 3372, 3222 and 2977 cm^{-1} (J) are assigned to the weakly hydrogen bonded water molecules (Å/cm^{-1}) 2.79/3392, 2.79/3381 and 2.73/3243 cm^{-1} (S), and 2.78/3361, 2.79/3372, 2.72/3222 cm^{-1} (J). According to Beran and Libowitzky [43-45], these bonds are over 2.70 Å and therefore may be characterized as weak hydrogen bonds. Very weak infrared shoulders at 3554 cm^{-1} (S) and 3554 and 2977 cm^{-1} are not discussed. No Raman bands were observed in the region of bending vibrations of water molecules, however, infrared bands at 1624 cm^{-1} (S) and 1631 cm^{-1} (J) are assigned to the δ (ν_2) bending vibrations of water molecules. Raman bands at 1588 and 1513 cm^{-1} (S) and 1594 and 1511 cm^{-1} (J) are characterized as combination bands [42].

CONCLUSIONS

(1) Raman and infrared spectra of two mixite samples from Czech localities, containing ~0.30 P^{5+} apfu, were studied.

(2) The spectra of both mineral samples are practically very similar, some differences may be inferred in the organization of their hydrogen bonding network. Some

differences in band positions and intensities may be caused by different ratios of $(AsO_4)^{3-}$, $(AsO_3OH)^{2-}$, $(PO_4)^{3-}$ and $(PO_3OH)^{2-}$ in the structure of studied mixite samples.

(3) Observed Raman and infrared bands were assigned to the stretching nad bending vibrations of $(AsO_4)^{3-}$, $(AsO_3OH)^{2-}$, $(PO_4)^{3-}$ and $(PO_3OH)^{2-}$ units, hydroxyl ions and water molecules.

(4) O-H…O hydrogen bond lengths were inferred from both Raman and infrared ν OH stretching vibrations. Hydrogen bond lengths are over 2.70 Å and may be therefore characterised as weak.

Acknowledgements

The financial and infrastructure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the Raman and infrared spectrometers. This work was financially supported by Ministry of Culture of the Czech Republic (DE07P04OMG004) to Jiří Sejkora and Jakub Plášil.

REFERENCES

1. Sejkora J, Řídkošil T, Šrein V *Neues Jahr. Min.* **1999**, *175*, 105-124.
2. Walenta K, Theye T *Aufschluss* **2004**, *55*, 17-23.
3. Walenta K, Theye T *Neues Jahr. Min.* **2005**, *181*, 219-222.
4. Sejkora J, Novotný P, Novák M, Šrein V, Berlepsch P *Can. Min.* **2005**, *43*, 1393-1400.
5. Walenta K *Erzgräber* **2003**, 17, 46-51.
6. Olmi F, Sabelli C, Trosti Ferroni R *Neues Jahr. Min.* **1991**, 487-499.
7. Sejkora J, Šrein V *Zprávy o geologických výzkumech v roce 1995*, **1996**, 153-155.
8. Dietrich JE, Orliac M, Permingeat F *Bull. Soc. Franc. Min. Crist.* **1969**, *92*, 420-34.
9. Aruga A, Nakai I *Acta Cryst.* **1985**, *C41*, 161-3.
10. Mereiter K, Preisinger A *Öst. Akad. Wissen., math.-naturwiss. Kl*. **1986**, *123*, 79-81.
11. Zemann J *Mitteilungen der Österreichischen Mineralogischen Geselschaft* **1991**, *136*, 21-34
12. Miletich R, Zemann J *Aufschluss* **1993**, *44*, 17-21.
13. Miletich R, Zemann J, Nowak M *Phys. Chem. Min.* **1997**, *24*, 411-422.
14. Schrauf A *Zeit. Kryst.* **1880**, *4*, 277-281.
15. Frost RL, Weier M, Martens W, Duong L *Min. Mag.* **2005**, 69, 169-177.
16. Frost RL, Weier M. Martens W *Spectrochim. Act.* **2006**, *A63*, 60-65
17. Frost RL, Mckinnon AR, Williams PA, Erickson KL, Weier ML, Leverett P *Neues Jahr. Min.* **2005**, *181*, 11-19.
18. Frost RL, Erickson KL, Weier ML, McKinnon AR, Williams PA, Leverett P *J. Raman Spectrosc.* **2004**, *35*, 961-966.
19. Frost RL, Weier M, Martens WN *Spectrochim. Act.* **2006**, *63*, 685-689.
20. Frost RL, Čejka J, Ayoko GA, Dickfos MJ *J. Raman Spectrosc.* **2008**, *39*, 374-379.
21. Frost RL, Čejka J, Dickfos MJ *J. Raman Spectrosc.* **2008**, *39*, 779-785.
22. Frost RL, Čejka J, Keeffe EC, Dickfos MJ *J. Raman Spectrosc.* **2008**, *39*, 1413-1418
23. Frost RL, Dickfos MJ, Čejka J *J. Raman Spectrosc.* **2008**, *39*, 1158-1161.
24. Frost RL, Dickfos MJ, Čejka J *J. Raman Spectrosc.* **2008**, *39*, 582-586.
25. Frost RL, Dickfos MJ, Reddy BJ *J. Raman Spectrosc.* **2008**, *39*, 1250-1256.
26. Frost RL, Hales MC, Wain DL *J. Raman Spectrosc.* **2008**, *39*, 108-114.
27. Frost RL, Keeffe EC *J. Raman Spectrosc.* **2008**, *39*, 1408-1412.
28. Sejkora J, Gabašová A, Novotná M *Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze* **1997**, *4-5*, 185-187

29. Plášil J, Sejkora J, Čejka J, Škoda R, Goliáš V *J. Geosc.* **2009**, *54*, 15-56.
30. Frost RL, Čejka J, Dickfos MJ *J. Raman Spectrosc.* **2009**, *40*, 38-41.
31. Frost RL, Keeffe EC *J. Raman Spectrosc.* **2009**, *40*, 42-45.
32. Frost RL, Keeffe EC *J. Raman Spectrosc.* **2009**, *40*, 133-136.
33. Frost RL, Keeffe EC *J. Raman Spectrosc.* **2009**, *40*, 128-132.
34. Ross SD *Inorganic Infrared and Raman Spectra (European Chemistry Series)*, **1972**.
35. Siebert H *Z. Anorg. u. allgem. Chem.* **1954**, *275*, 225-40.
36. Vansant FK, Van der Veken BJ *J. Mol. Struc.* **1973**, *15*, 439-44.
37. Vansant FK, Van der Veken BJ, Desseyn HO *J. Mol. Struc.* **1973**, *15*, 425-37.
38. Myneni SCB, Traina SJ, Waychunas GA, Logan TJ *Geochim. Cosmochim. Acta* **1998**, *62*, 3499-3514.
39. Myneni SCB, Traina SJ, Waychunas GA, Logan TJ *Geochim. Cosmochim.Acta* **1998**, *62*, 3285-3300.
40. Nakamoto K *Infrared and Raman spectra of inorganic and coordination compounds.* J. Wiley and Sons, New York 1986.
41. Keller P *Neues Jb. Miner. Mh.* **1971**, 491-510.
42. Pechkovskii VV, Melnikova PY, Dzyuba ED, Baranikova TI, Nikanovich MV, *Atlas of infrared spectra of phosphates. Orthophosphates.* Nauka Moscow 1981. (in Russian)
43. Libowitzky E, *Monatshefte für Chemie* **1999**, *130,* 1047-1059.
44. Beran A, Libowitzky E, *IR spectroscopy and hydrogen bonding in minerals.* In *Microscopic Properties and Processes in Minerals* (K. Wright & R. Catlow, Eds.), p. 493-508, Kluwer Academic Publishers. Dordrecht, The Netherlands.
45. Libowitzky E, Beran A EMU Notes in Mineralogy **2006**, *6*, 227-279, Eötvös University Press, Budapest.

List of Figs.

Fig. 1 Raman spectra of mixite from Smrkovec and Jáchymov in the 700 to 1200 cm^{-1} region.

Fig. 2 Infrared spectra of mixite from Smrkovec and Jáchymov in the 600 to 1200 cm^{-1} region.

Fig. 3 Raman spectra of mixite from Smrkovec and Jáchymov in the 100 to 700 cm^{-1} region.

Fig. 4 Raman spectra of mixite from Smrkovec and Jáchymov in the 1200 to 3700 cm^{-1} region.

Fig. 5 Infrared spectra of mixite from Smrkovec and Jáchymov in the 1200 to 3800 cm^{-1} region.

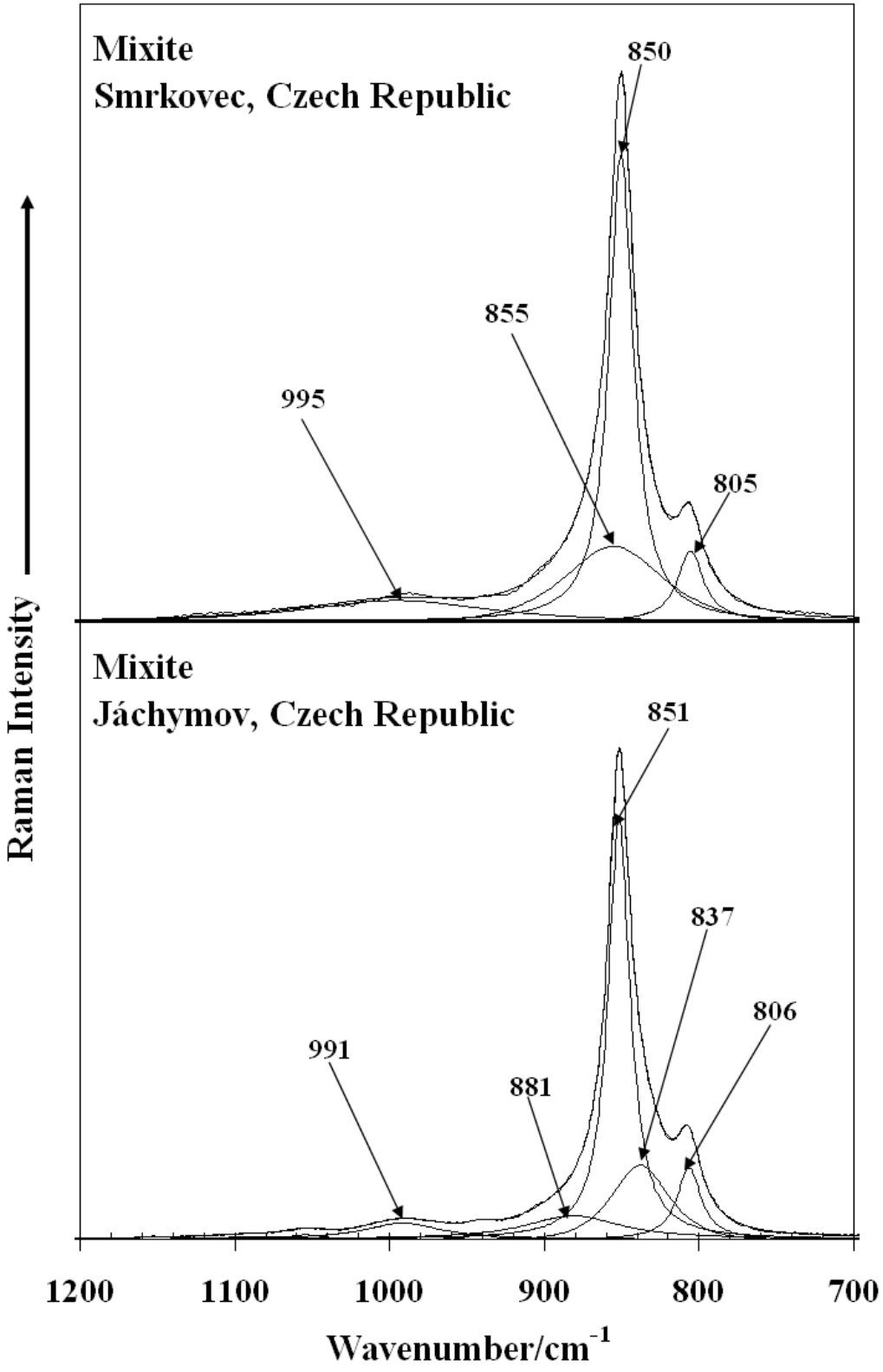
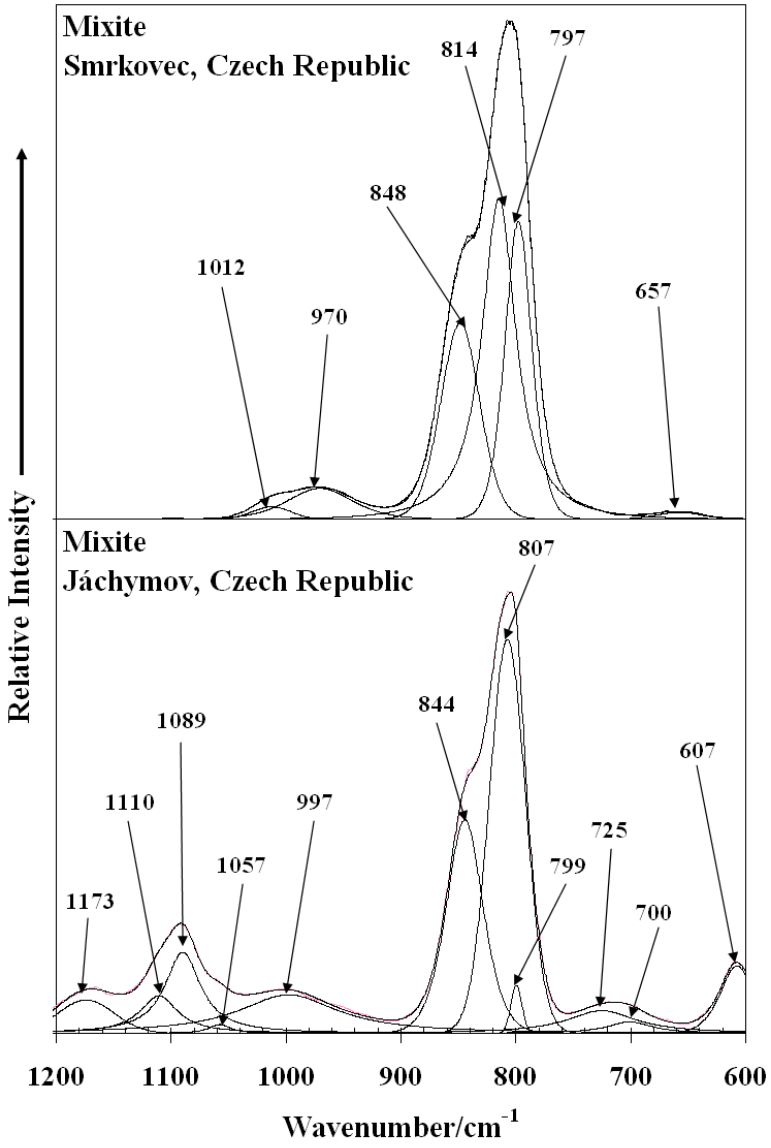

Mixite
Smrkovec, Czech Republic
850
855
995
805
Mixite
Jáchymov, Czech Republic
851
837
806
991
881
Raman Intensity
1200
1100
1000
900
800
700
Wavenumber/cm-1

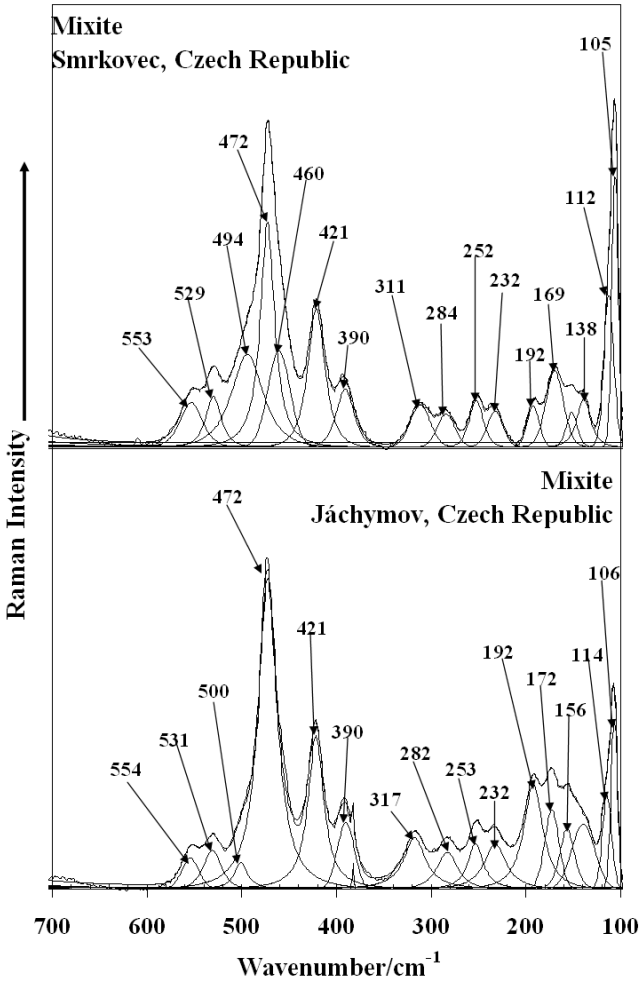
Fig. 1



343

344

345 **Fig. 2**



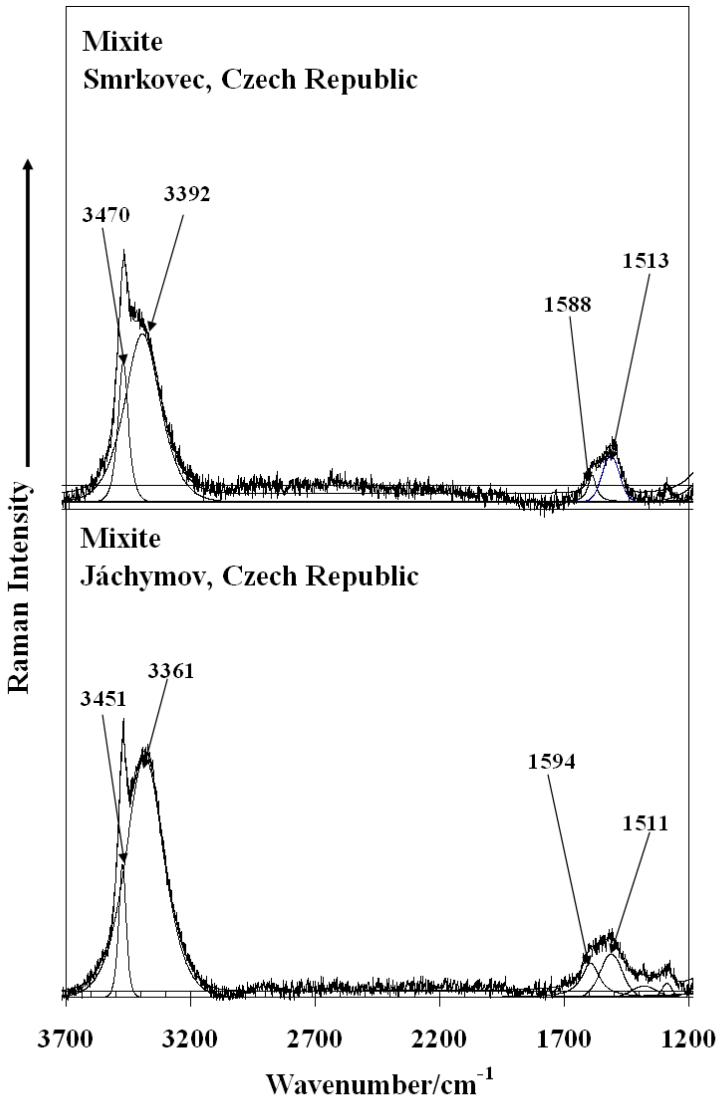
346

347

348 **Fig. 3**

349

350



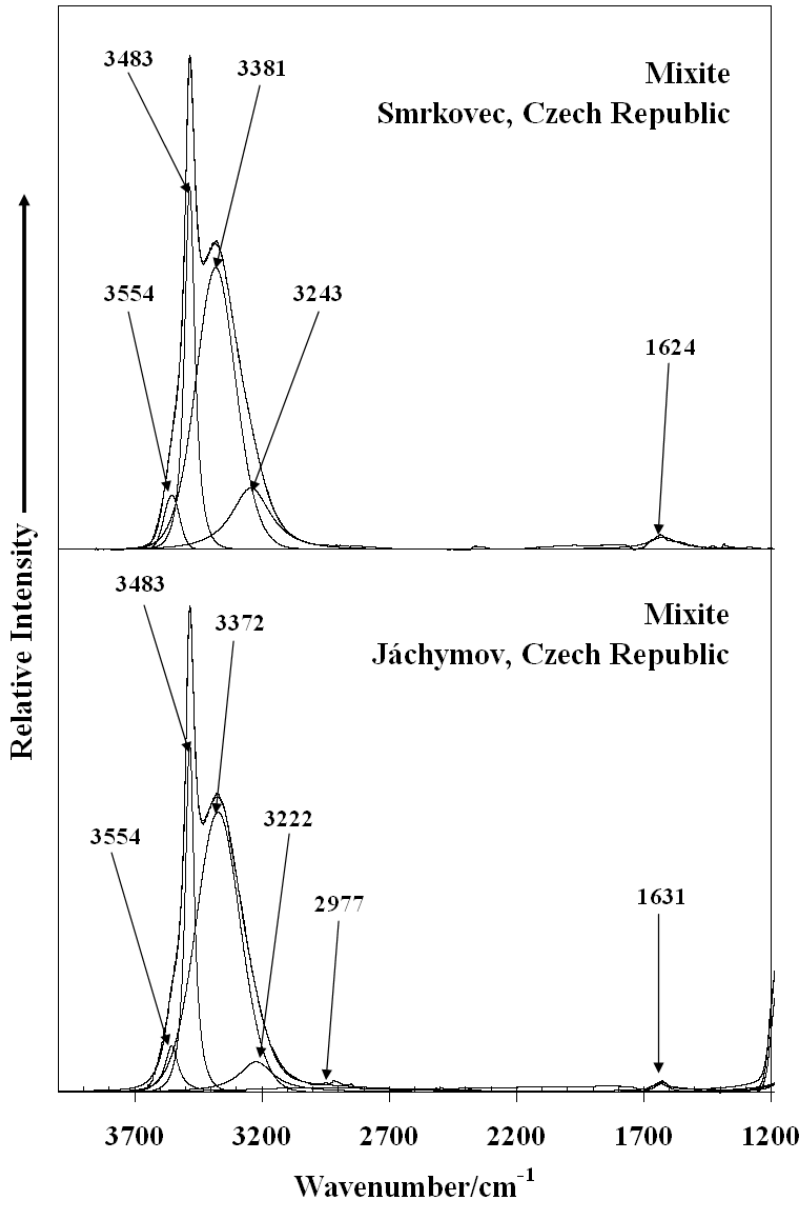
351

352

353 **Fig. 4**

354

355



356

357

358 **Fig. 5**

359