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Molecular structure of the uranyl mineral zippeite –An XRD, SEM and Raman spectroscopic study

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Abstract

Raman spectra at 298 and 77 K and infrared spectra of the uranyl sulfate mineral zippeite, $K_2[(UO_2)_6(SO_4)_3O(OH)_6] \cdot 4 H_2O$, were studied. Observed bands were tentatively attributed to the $(UO_2)^{2+}$ and $(SO_4)^{2-}$ stretching and bending vibrations, the OH stretching vibrations of water molecules and hydroxyls, H_2O bending vibrations and libration modes, and δ U-OH bending vibrations. Empirical relations were used for calculation of U-O bond lengths in uranyl $R = f(\nu_3 \text{ or } \nu_1 (UO_2)^{2+}) \text{ \AA}$. This was found in agreement with U-O bond lengths from the single crystal structure analysis. The number of observed bands supports the conclusion from single crystal structure analysis that at least two symmetrically distinct U^{6+} (in uranyl) and S^{6+} (in sulfate), and water molecules and hydroxyls may be present in the zippeite crystal structure. Some O-H...O bond lengths were attributed to the hydrogen-bonding network in zippeite crystal structure.

Keywords: zippeite, potassium uranyl sulfate mineral, chemical formula, infrared and Raman spectroscopy, U-O bond length, O-H...O bond lengths

Introduction

Uranyl sulfate minerals are widespread around uranium bearing mine sites, where they usually form during the evaporation of acid sulfate-rich mine drainage waters (BRUGGER et al. 2003; FINCH & MURAKAMI 1999). They typically occur close to actively oxidizing uraninite and sulfide minerals (SMITH 1984). Uranyl sulphates usually occur as admixtures of species consisting of fine-grained mats and coatings, making their characterization difficult (ANTHONY et al. 2003; BURNS et al. 2003; FRONDEL 1958; FRONDEL & WEEKS 1958).

The chemistry of the zippeite group minerals has been controversial since the naming of the first member of this group by Haidinger in 1845 (BRUGGER et al. 2003). Zippeite group minerals have been understood for a long time as phases, containing only UO_3 , SO_3 , and H_2O (FRONDEL et al. 1976; FRONDEL & WEEKS 1958; NOVACEK 1935). FRONDEL & WEEKS (1958) published a short report, in which they wrote "one of the oldest and most complicated problems in the descriptive mineralogy of uranium has been the constitution and identity of the natural uranyl sulfates, in particular those of the so-called zippeite type". According to these authors, zippeites are not simple hydrated uranyl sulfates, but in fact each of them contains a cation in addition to the uranyl ion. The additional cation found from their study of synthetic and natural phases is either K, NH_4 , Na, Co, Ni, Fe, Mg, or Zn. The compounds fall into three subgroups of isostructural members: (a) The K and NH_4 members, forming a complete solid solution series; (b) the Na member; (c) the Co, Ni, Fe, Mg and Zn members which form a complete series between Co and Ni and probably between these elements and all of the other cations listed. Some details of this research were published later in 1976 (FRONDEL et al. 1976) including chemical analysis, X-ray powder pattern and indices of refraction. The original zippeite from Jáchymov (Czech

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Republic) was found to contain K^+ ions and FRONDEL et al. (1976) proposed to retain and restrict the name zippeite to this mineral species. Unfortunately, inventory numbers of the zippeite samples from the collections of the Department of Mineralogy and Petrology, Natural History Museum, National Museum Prague, Czech Republic studied by FRONDEL et al. (1976) are not known. The other zippeites are called e.g. Na-zippeite and Mg-zippeite. On the basis of these results, the formula of zippeite was given as $K_4[(UO_2)_6(SO_4)_3(OH)_{10}] \cdot 4 H_2O$ (FRONDEL et al. 1976).

O'BRIEN & WILLIAMS (1981) studied the free energy of formation ΔG_f° of synthetic zippeite, the formula of which was the same as described by FRONDEL et al. (1976). Because of some discrepancies in the composition of zippeites, VOCHTEN et al. (1995, 1997) described X-ray powder pattern, unit cell parameters, single crystal structure analysis and other physicochemical characteristics of synthetic zippeite of the composition $K[(UO_2)_2(SO_4)(OH)_3] \cdot H_2O$, inclusive IR spectrum (VOCHTEN et al. 1997; VOCHTEN et al. 1995). BRUGGER et al. (2003) modified this formula to $K[(UO_2)_2(SO_4)O_2] \cdot 2 H_2O$. Bond-valence analysis of the crystal structure proposed by VOCHTEN et al. (1995) leads to the formula $K[(UO_2)_2(SO_4)O_2] \cdot 2 H_2O$ – this is the modified formula by BRUGGER et al. (2003), which is not neutral (BURNS et al. 2003). MEISSER (2003) formulates Vochten's synthetic zippeite as $[K(H_2O)][(UO_2)_2(SO_4)O(OH)] \cdot H_2O$ which is electro-neutral. There is an important fact in the case of zippeite mineral group. Molar ratio $(UO_2)^{2+}/(SO_4)^{2-}$ remains constant in all known natural and synthetic zippeites and is 2. ČEJKA (1999 and references therein) reviewed all available data on IR spectrum and thermal analysis of zippeites, inclusive those of proper zippeite (K-zippeite) and confirmed that there are at least two structurally distinct subgroups of natural and synthetic zippeites (ČEJKA 1999). ONDRUŠ et al. (1997) shortly described zippeite sample from Jáchymov and its X-ray powder pattern and unit cell parameters (ONDRUŠ et al. 2003; ONDRUŠ et al. 1997). SEJKORA et al. (2003) discussed some minerals of the zippeite group from Janská vein, Březové hory Mts., Příbram (Czech Republic) and X-ray powder pattern of a mixture of zippeite and Na-zippeite. Most crystal structures of natural and synthetic uranyl sulfates may be influenced by pressure and temperature changes caused by grinding, rubbing or pressing of microcrystals e.g. for KBr disk preparation (ČEJKA 1999). Indeed this is a good reason to use Raman spectroscopy to study uranyl compounds. It is therefore very probable that especially hydrogen-bonding network of hydrothermally synthesized zippeites may differ from those prepared at room temperature and may be also from zippeites formed in nature under supergene oxide zone conditions. Neither an exact quantitative chemical nor single crystal structure analysis for natural zippeite is available.

Uranyl sulfate solid state and solution chemistry plays one of the most important roles in the actinide chemistry, mineralogy, geochemistry and “environmental chemistry” with regard to uranium(VI) migration in natural waters and to spent nuclear fuel problems. As a part of our on-going research into secondary mineral formation and the analysis of the molecular structure of these minerals, we report the vibrational spectra of the zippeite sample and relate to the mineral structure.

Experimental

Minerals

Zippeite sample from the Happy Jack Mine, White Canyon, San Juan County, Utah, U. S. A., was investigated. The zippeite mineral used in this work was obtained from Museum Victoria. X-ray powder pattern and EDAX analysis of the mineral was carried out for their determination.

X-ray diffraction

X-ray diffraction (XRD) patterns were recorded using $CuK\alpha$ radiation ($n = 1.5418\text{Å}$) on a Philips PANalytical X'Pert PRO diffractometer operating at 40 kV and 40 mA with 0.125° divergence slit, 0.25° anti-scatter slit, between 3 and 15° (2θ) at a step size of 0.0167° . For low angle XRD, patterns were recorded between 1 and 5° (2θ) at a step size of 0.0167° with variable divergence slit and 0.5° anti-scatter slit.

SEM and X-ray microanalysis

Zippeite samples were coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at 25kV accelerating voltage. Preliminary analyses of the zippeite samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the

clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system. Uranium oxide was used as a standard for U. The K-K α peak is strongly overlapped by the U-M lines and was deconvolved using a peak strip routine, which gave similar results to a peak fit routine used by the EDAX analysis software. However some uncertainty remains in the quantitative measurements of K in the presence of U. Oxygen was not measured directly but was calculated using assumed stoichiometries to the other elements analysed.

Raman microprobe spectroscopy

The crystals of zippeite mineral was placed and orientated on the stage of an Olympus BHS microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm⁻¹ in the range between 100 and 4000 cm⁻¹. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the techniques which have been applied to the study of uranyl compounds have been published by the authors (FROST RAY 2004; FROST RAY & WEIER 2004; FROST 2004; FROST et al. 2004a; FROST et al. 2004b; FROST & WEIER 2004; FROST et al. 2004c).

Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm⁻¹ range were obtained by the co-addition of 64 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s.

Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Results and discussion

X-ray diffraction

The results of the analysis including peak position, peak intensity, peak widths and d-spacing are reported in Table 1. The analysis confirms the mineral as zippeite with a trace of gypsum. Unit cell parameters of synthetic monoclinic zippeite are a 8.755(3), b 13.987(7), c 17.730(7) Å, β 104.13(3)° (ONDRUS et al. 1997) and a 8.7524(4), b 13.9197(7), c 17.6972(8) Å, β 104.178(1)° (SEJKORA et al. 2003), and for natural zippeite a 8.740(3), b 14.157(5), c 17.722(5) Å, β 104.28(3)° (VOCHTEN et al. 1995), or a 8.656(2), b 14.240(4), c 17.706(5) Å, β 104.112(1)° (BURNS et al. 2003). Unit cell parameters of the USA zippeite studied in this work are a = 8.626(0), b = 14.198(3), c = 17.627(4) Å, α = 90°, β = 102.52(9)°, γ = 90°. The unit cell parameters of the Happy Jack zippeite are close to those values for the synthetic zippeite and to a natural zippeite.

EDX analyses

SEM images reveal that the zippeite morphology consists of an array of rosettes of flat elongated crystals. The rosettes are up to 50 μ m in diameter (Figures 1a,b,c) while individual crystals are up to 20 μ m in length and less than 0.5 μ m in thickness (Figure 2b). Figure 1d shows a backscattered electron image of an embedded rosette in cross-section. Quantitative analyses of four clusters of crystals in the polished zippeite sample from Happy Jack Mine, USA, are shown in Table 2. Calculation of atomic ratios from these results give an average stoichiometry for K : U : S of 0.67 : 2.04 : 1. On the basis of the analysis results, the empirical formula of the zippeite sample is (K₂O)_{0.969}(MgO)_{0.06}(Al₂O₃)_{0.124}(FeO)_{0.03}(UO₃)₆(SO₃)_{2.944}(SiO₂)_{0.08} · 5.78 H₂O

The ideal formula of this zippeite sample studied is therefore K₂[(UO₂)₆(SO₄)₃O(OH)₆] · 4 H₂O, which is closer to the formula proposed by Frondel et al. (1976) with the exception of lower content of K⁺ ions, and partly differs from the formulas of synthetic zippeites given by (VOCHTEN et al. 1997)– K[(UO₂)₂(SO₄)(OH)₃] · H₂O, (BRUGGER et al. 2003)– K[(UO₂)₂(SO₄)O₂] · 2 H₂O, (MEISSER 2003)– K(H₂O)[(UO₂)₂(SO₄)O(OH)] · H₂O, and (BURNS et al. 2003)– K₃(H₂O)₃[(UO₂)₄(SO₄)₂O₃(OH)]. These differences may be caused by various

conditions of origin or synthesis of mentioned zippeites. Important is the fact, that only small differences may be observed in $(\text{UO}_2)^{2+}/(\text{SO}_4)^{2-}/(\text{O})^{2-}/(\text{OH})^-$ layers. This means that all these layers have very similar uranyl anion topology with the molar ratio $(\text{UO}_2)^{2+}/(\text{SO}_4)^{2-} = 2$ (BURNS 1999; BURNS et al. 1996), but differ for necessary charge balance in the composition of the interlayer space. As described above, the formula of zippeite sample corresponds to $\text{K}_2[(\text{UO}_2)_6(\text{SO}_4)_3\text{O}(\text{OH})_6] \cdot 4 \text{H}_2\text{O}$, which is relatively closer to the formula proposed by FRONDEL et al. (1976) than to the formulas of synthetic zippeites prepared by VOCHTEN et al. (1995) and Burns et al. (2003). However, the studied zippeite sample has a lower content of K^+ ions than that described by FRONDEL et al. (1976) (FRONDEL et al. 1976).

Synthetic zippeites possess symmetrically distinct U^{6+} and S^{6+} (2 + 2 in Vochten's synthetic zippeite, 4 + 2 in Burns's zippeite, respectively) in their crystal structures. Interpretation of the IR and Raman spectra of zippeite sample studied is therefore done respecting that in its crystal structure may be present symmetrically distinct U^{6+} and S^{4+} .

Infrared and Raman spectroscopy

The IR (298 K) and Raman spectra (298 and 77 K) of the zippeite are shown in Figures 2-4 and Table 3. From the X-ray single crystal structure analysis may be inferred that symmetries of free uranyl ($D_{\infty h}$) and sulfate (T_d) are lowered. All vibrations may be therefore IR and Raman active and their number enhanced because of the presence of symmetrically distinct groups in the crystal structure, splitting of degenerate vibrations, and also respecting the factor group analysis.

Two bands observed in the region $1003 - 1016 \text{ cm}^{-1}$ [IR 1012 and 1003 cm^{-1} ; Raman 1014 and 1009 cm^{-1} (298 K) and 1016 and 1011 cm^{-1} (77 K)] are attributed to the $\nu_1 (\text{SO}_4)^{2-}$ symmetric stretching vibrations. Bands observed in the region $1067 - 1176 \text{ cm}^{-1}$ [IR 1176, 1141, 1116, 1101 and 1068 cm^{-1} ; Raman 1151, 1124 and 1096 cm^{-1} (298 K), 1155 and 1098 cm^{-1} (77 K)] may be assigned to the $\nu_3 (\text{SO}_4)^{2-}$ antisymmetric stretching vibrations. The observation of multiple bands in this region can be accounted for by the lowering of the symmetry of the $(\text{SO}_4)^{2-}$ units or the presence of symmetrically distinct $(\text{SO}_4)^{2-}$ units or factor group influence. However, there may be also some coincidence with the δ U-OH bending vibrations. Differences between the positions of bands connected with the $\nu_3 (\text{SO}_4)^{2-}$ observed in this paper and previously published data (CEJKA 1999) may be accounted for by the difference in the samples. The spectra in this paper were obtained from natural zippeite sample. Published data originated from the spectra from synthetic samples. It is noted that considerable variation in the spectra results because of variations in the crystal structure of the mineral which results from the different methods for the synthesis of the zippeite. Natural zippeite is not the same as a synthetic zippeite. This may be also connected with relatively labile crystal structures of natural and also some synthetic uranyl sulfates (CEJKA 1999).

Intense bands in the region $810 - 850 \text{ cm}^{-1}$ may be assigned to the $\nu_1 (\text{UO}_2)^{2+}$ symmetric stretching vibrations [Raman 846, 827 and 810 cm^{-1} (298 K) and 841, 830 and 813 cm^{-1} (77 K); IR 851 and probably also 799 cm^{-1}]. Splitting of the bands in Raman spectrum support that symmetrically distinct uranyls are present in the crystal structure of zippeite sample studied. Bands observed in the region $864 - 890 \text{ cm}^{-1}$ are attributed to the $\nu_3 (\text{UO}_2)^{2+}$ antisymmetric stretching vibrations [Raman 888 and 881 cm^{-1} (298 K) and 864 cm^{-1} (77 K); IR 890 cm^{-1}]. Some coincidences of the ν_1 and $\nu_3 (\text{UO}_2)^{2+}$ vibrations with δ U-OH vibrations cannot be excluded.

Wavenumbers of the $(\text{UO}_2)^{2+}$ stretching vibrations were used for the calculation of the U-O bond lengths in uranyl. Empirical relations by Veal et al. (BARTLETT & COONEY 1989; GLEBOV 1989; VEAL et al. 1975) gave the following results as reported in Table 4. The mean U-O bond length (uranyl) in the VOCHTEN's synthetic zippeite is $1.77(3) \text{ \AA}$ (VOCHTEN et al. 1995), and the mean U-O bond length (uranyl) in the BURNS's zippeite is 1.7805 \AA (BURNS et al. 2003). U-O bond lengths calculated from the wavenumbers of the observed $(\text{UO}_2)^{2+}$ stretching vibrations in the studied natural zippeite agree not only with the both mean values for synthetic zippeites, but also with the average U-O bond length $1.79(4) \text{ \AA}$ for uranyl pentagonal dipyramidal polyhedra UO_2O_5 typical for crystal structures of most uranyl natural and synthetic phases inclusive uranyl sulfate minerals (BURNS 1999; BURNS et al. 2003; BURNS et al. 1997; BURNS et al. 1996).

Bands observed in the IR spectra at 1665 , 1623 and 1614 cm^{-1} and those in the Raman spectra at 1629 (298 K) and 1597 (77 K) are attributed to the $\delta \text{H}_2\text{O}$ bending vibrations. The number of bands and their wavenumbers indicate that structurally distinct and nonequivalent water molecules are present in the crystal structure of studied zippeite sample bonded by differently strong hydrogen bonds. Bands at 1540 , 1423 and 1408 cm^{-1} (IR) and 1385 cm^{-1} (Raman 77 K) may be assigned to the δ U-OH bending vibrations. This observation supports the presence of $(\text{OH})^-$ ions in the crystal structure of zippeite. This also agrees with the crystal structures

of the both Vochten's and Burns's zippeites and also Meisser's formula for zippeite. For these crystal structures, U-OH bonds were inferred from the calculation of bond-valence parameters.

The Raman spectra of the low wavenumber region show bands connected with the ν_2 and ν_4 (SO_4)²⁻ bending vibrations. IR spectrum usually show only bands attributed to the ν_2 (SO_4)²⁻ bending vibrations (MYNENI 2000). Bands at 672, 623 and 581 cm^{-1} (IR), at 665, 612 and 556 cm^{-1} (Raman 298 K) and at 667 cm^{-1} (Raman, 77 K) are assigned to the ν_4 (SO_4)²⁻ bending vibrations, while bands at 511, 494, 473, 460, 417, and 406 cm^{-1} (Raman, 298 K) and 510, 506, 463, 428 and 409 cm^{-1} (Raman, 77 K) to the ν_2 (SO_4)²⁻ bending vibrations. Bands attributed to H_2O libration modes may be also observed in this region. Bands at 369 and 342 cm^{-1} (Raman, 298 K) and 377, 347 and 343 cm^{-1} (Raman, 77 K) are assigned to the ν $\text{U-O}_{\text{equatorial}}$, i. e. $\text{U-O}_{\text{ligand}}$ vibrations. Bands at 283 and 253 cm^{-1} (Raman, 298 K) and 281. and 262 cm^{-1} (Raman, 77 K) may be attributed to the δ (UO_2)²⁺ bending vibrations and those at lower wavenumbers (219.6, 198.5, 174.2 and 149.6 cm^{-1} , and 199.8, 176.7 and 150.9 cm^{-1} (Raman, 298 and 77 K, respectively) are connected with molecular deformation and lattice modes.

The Raman and IR spectra of the ν OH stretching vibrations of water molecules and (OH)⁻ ions are observed in the region 2800 – 3614 cm^{-1} . The number of the bands proves that structurally nonequivalent H_2O molecules and differently hydrogen bonded water molecules are present in the crystal structure of zippeite studied. This agrees with the bands observed in the region of bending vibrations of water molecules. Shoulders in the region 3500-3620 cm^{-1} prove that also only very weakly hydrogen bonded hydroxyls and/or water molecules are present in the crystal structure of zippeite sample studied. Using the (LIBOWITZKY 1999) correlation, O-H...O hydrogen bond lengths may be inferred. Their approximate values (\AA) in decreasing order of wavenumber are > 3.2, 3.154, 2.916, 2.808, 2.713, 2.660 and 2.616 (IR), 2.912, 2.835, 2.699 (Raman, 298 K), and 2.772, 2.7155, 2.673 (Raman, 77 K).

Conclusions

Raman spectroscopic study together with the study of the IR spectra has enabled a study of the uranyl mineral zippeite. Chemical composition of this zippeite sample, $\text{K}_2[(\text{UO}_2)_6(\text{SO}_4)_3\text{O}(\text{OH})_6] \cdot 4 \text{H}_2\text{O}$, is closer to the formula proposed for natural zippeite by FRONDEL et al. (1976) and also somewhat different from the zippeite synthetic analogues hydrothermally prepared by VOCHTEN et al. (1995) and BURNS et al. (2003). However, K^+ ions content in zippeite sample, studied in this paper, is lower than that in Frondel's zippeite. The uranyl anion sheet topology is very similar in all these zippeites and the molar ratio $(\text{UO}_2)^{2+}/(\text{SO}_4)^{2-}$ remains always 2:1. Some differences may be observed in the interlayer space. The reason for somewhat different arrangements discussed in one natural and two synthetic phases may be that natural zippeite has been the most probably formed in the supergene under low temperature, while both synthetic zippeites have been synthesized hydrothermally. Hydrogen-bonding network may be strongly influenced by conditions of formation. This may cause some rearrangements of the crystal structure of natural uranyl sulfates like zippeite.

U-O bond lengths in uranyl, calculated with some empirical relations from the wavenumbers of the uranyl stretching vibrations are in agreement with the bond lengths inferred from known single crystal structure analysis of synthetic zippeites. Numbers of the bands assigned to the $(\text{UO}_2)^{2+}$ stretching vibrations and the $(\text{SO}_4)^{2-}$ bending and stretching vibrations support the conclusion that symmetrically different uranyl and sulfate ions are present in the zippeite crystal structure as also inferred from the single crystal structure of synthetic zippeites.

As known also via thermal analysis (ČEJKA 1999), Raman and IR spectroscopy confirmed that weakly to strongly hydrogen bonded structurally nonequivalent water molecules and probably also hydroxyls are present in the crystal structure of zippeite. As known via X-ray single crystal structure analysis of synthetic zippeites, and also infrared and thermal analysis of some zippeites, it was confirmed in this paper with Raman and IR spectroscopy that weakly to strongly hydrogen bonded structurally nonequivalent water molecules and most probably also hydroxyls are present in uranyl sulfate sheets of zippeite.

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Table 1 Peak List of the X-ray diffraction pattern of zippeite

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
10.3130	1099.38	0.0590	8.57773	14.36
11.6523	1405.43	0.0590	7.59464	18.36
12.3200	6836.39	0.0984	7.18453	89.32
12.5300	7654.22	0.1181	7.06458	100.00
16.2350	76.92	0.4723	5.45976	1.00
20.7031	315.31	0.1181	4.29043	4.12
23.4200	127.35	0.0787	3.79850	1.66
24.8218	530.16	0.1968	3.58707	6.93
25.2152	844.72	0.1771	3.53199	11.04
25.5919	272.17	0.1378	3.48085	3.56
26.6061	75.47	0.2362	3.35042	0.99
28.5976	173.48	0.2755	3.12147	2.27
31.2574	702.42	0.0984	2.86166	9.18
33.8876	131.53	0.5510	2.64533	1.72
36.2100	28.81	0.4723	2.48082	0.38
38.1910	47.79	0.3149	2.35657	0.62
46.8662	29.75	0.7872	1.93859	0.39
52.4382	31.65	0.5760	1.74353	0.41

Table 2. Elemental concentrations in weight % from EDX analyses of crystal clusters from the zippeite sample from Happy Jack Mine, USA. Oxygen was calculated indirectly by stoichiometry.

Analysis	O	Mg	Al	Si	S	K	Ca	Fe	U
1	24.58	0.14	0.35	0.06*	4.33	3.80	0.00*	0.22	66.49
2	23.47	0.13	0.44	0.06*	4.43	3.09	0.06*	0.31	68.01
3	26.27	0.00	0.23	0.20	4.37	3.62	0.00*	0.02*	65.29
4	28.04	0.00	0.21	0.08*	4.28	3.67	0.02*	0.08*	63.59

* not significantly above background

Table 2 Analysis of zippeite using EDX analyses

ATR-IR			298K Raman			77K Raman		
Center	FWHM	Area	Center	FWHM	Area	Center	FWHM	Area
3613.7	48.1	0.009						
3579.1	71.9	0.032						
3513.5	107.8	0.069	3510.9	111.9	0.010	3492.3	166.0	0.023
3414.1	189.0	0.151	3446.8	208.4	0.007			
3227.2	168.5	0.149	3184.7	247.6	0.036	3222.9	280.6	0.036
3049.1	251.3	0.166				3094.7	35.8	0.016
2829.8	161.1	0.024						
1665.2	74.7	0.003						
1622.8	14.9	0.001						
1614.3	59.1	0.022	1629.3	78.7	0.006	1596.8	118.0	0.058
1539.8	53.0	0.002						
1422.7	51.9	0.032						
1407.6	16.0	0.001				1384.5	203.5	0.064
1175.7	35.2	0.006	1151.0	49.6	0.004	1155.2	38.7	0.003
1140.7	54.6	0.076	1123.7	23.2	0.001			
1116.2	15.2	0.002						
1100.7	22.8	0.011	1095.5	32.0	0.026	1098.0	25.0	0.083
1067.6	50.1	0.091						
1011.9	88.4	0.028	1014.2	8.7	0.012	1016.2	6.6	0.049
1003.4	16.8	0.001	1009.3	18.5	0.015	1011.7	13.9	0.031
890.1	56.7	0.046	888.2	1.0	0.000			
			880.7	26.2	0.003	864.4	51.0	0.016
850.6	65.5	0.022	845.7	18.5	0.015	841.1	11.0	0.022
			827.3	14.5	0.188	830.4	12.8	0.173
798.6	99.8	0.009	810.2	33.7	0.087	812.9	29.2	0.084
795.6	31.9	0.002						
672.0	14.9	0.001	665.2	36.3	0.002	667.4	15.1	0.004
622.9	12.4	0.004	611.5	21.5	0.004			
580.5	8.6	0.003	556.0	24.6	0.001			
			510.7	25.2	0.006	509.7	15.8	0.003
			494.2	115.3	0.037	505.7	84.6	0.071
			472.9	15.5	0.002			
			460.1	16.9	0.017	463.3	23.6	0.087
			417.0	33.0	0.015	428.2	16.4	0.006
			405.6	21.8	0.172	409.4	16.3	0.081
			368.8	19.0	0.003	377.1	26.0	0.013
						346.9	26.1	0.014
			341.6	157.7	0.050	343.1	5.6	0.000
			282.8	23.1	0.015	281.1	19.8	0.010
			253.4	37.4	0.046	261.9	23.7	0.028
			219.6	15.8	0.006			
			198.5	41.0	0.035	199.8	36.7	0.013
			174.2	18.8	0.006	176.7	10.8	0.002
			149.6	19.7	0.005	150.9	8.5	0.002

Table 3 Results for the IR and Raman data for zippeite from Happy Jack Mine

ν_3 cm^{-1}	IR	Raman 298 K	Raman 298 K	Raman 77 K
	890.1	888.2	880.7	864.4
(VEAL et al. 1975)	1.773 Å	1.775 Å	1.779 Å	1.790 Å
(BARTLETT & COONEY 1989)	1.792 Å	1.793 Å	1.799 Å	1.811 Å
(GLEBOV 1989)	1.787 Å	1.788 Å	1.792 Å	1.802 Å
ν_1 cm^{-1}	IR	Raman 298 K	Raman 298 K	Raman 77 K
	850.4/798.6	845.7/827.3/810.2	841.1/830.4	812.9
(BARTLETT & COONEY 1989)	1.761 Å 1.812 Å	1.766 Å 1.783 Å 1.800 Å	1.770 Å 1.780 Å	1.790 Å

Table 4

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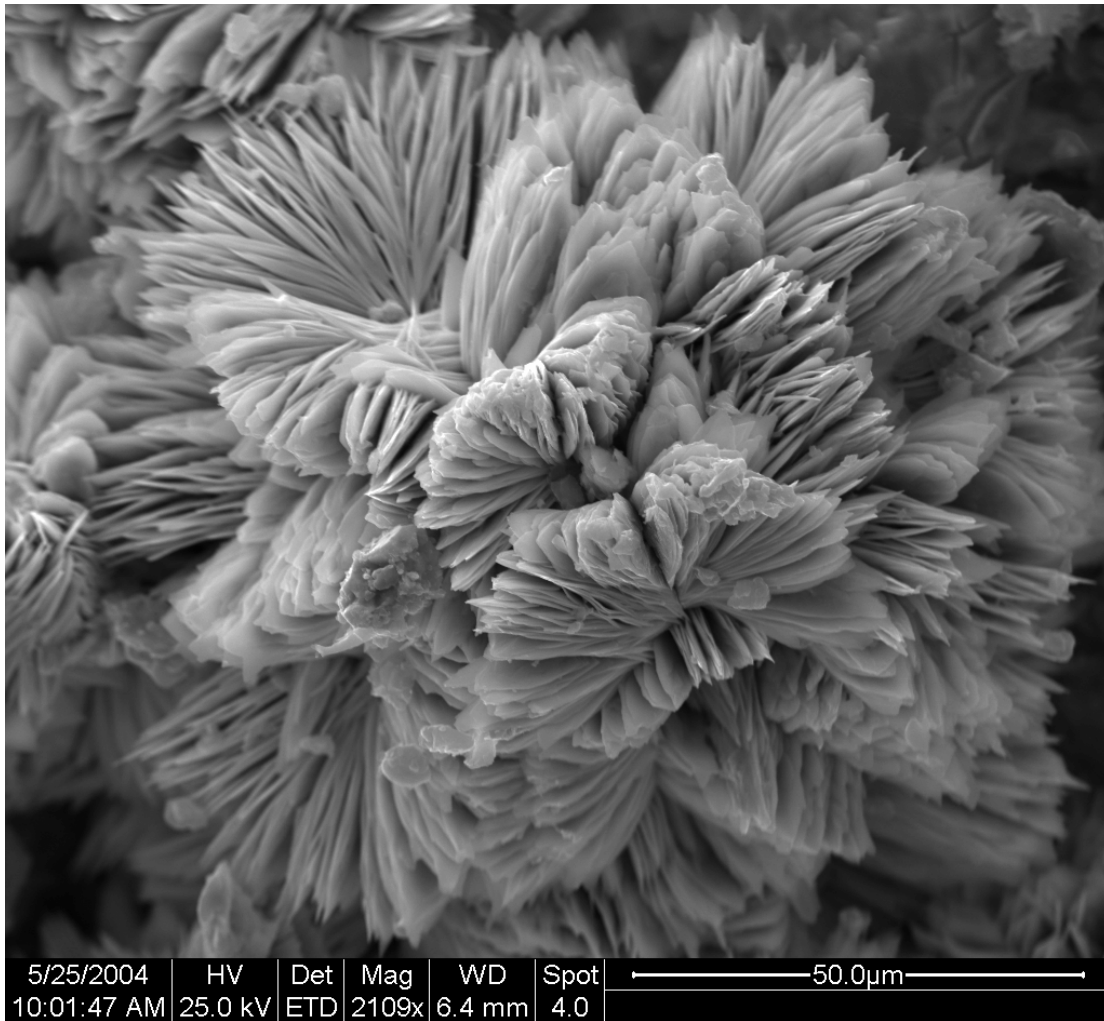


Figure 1a

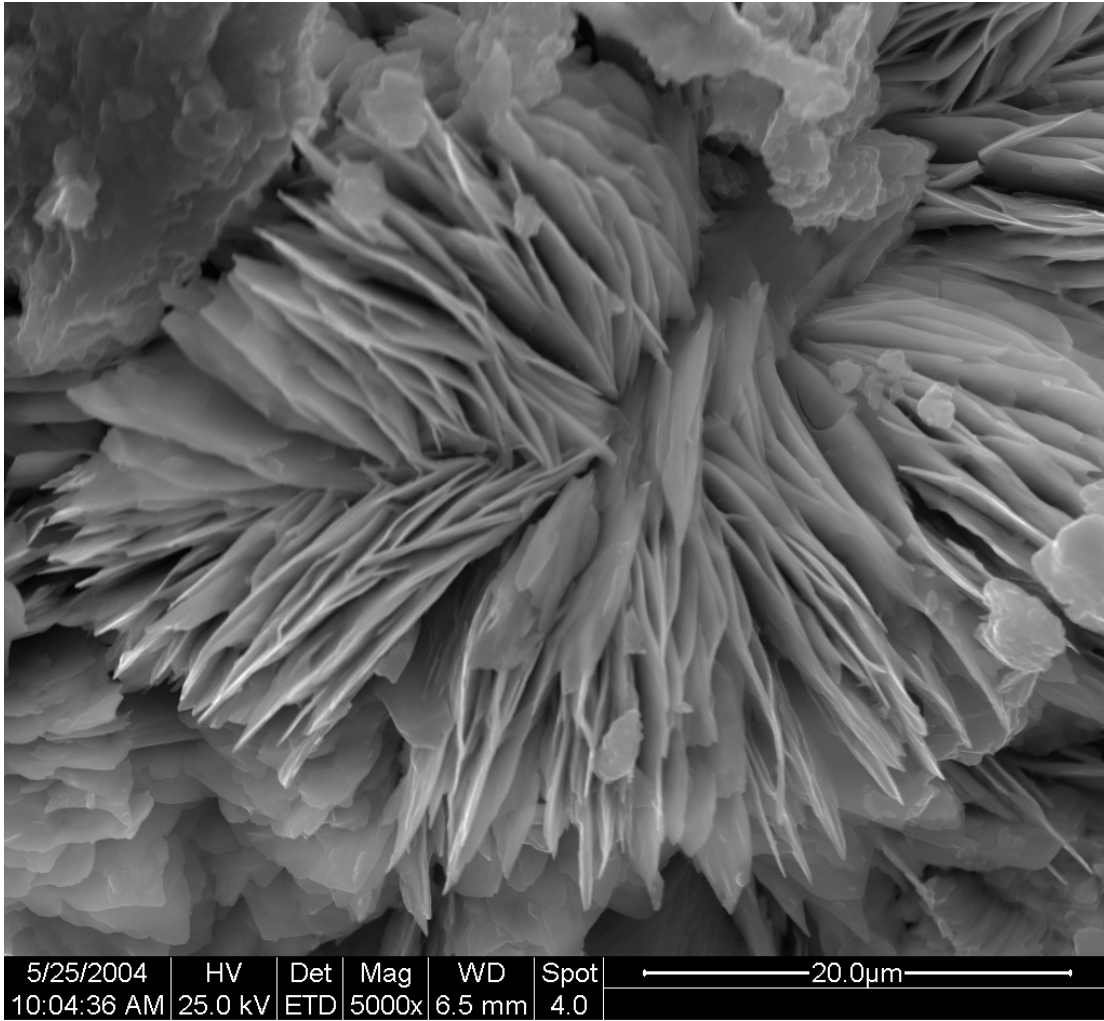


Figure 1b

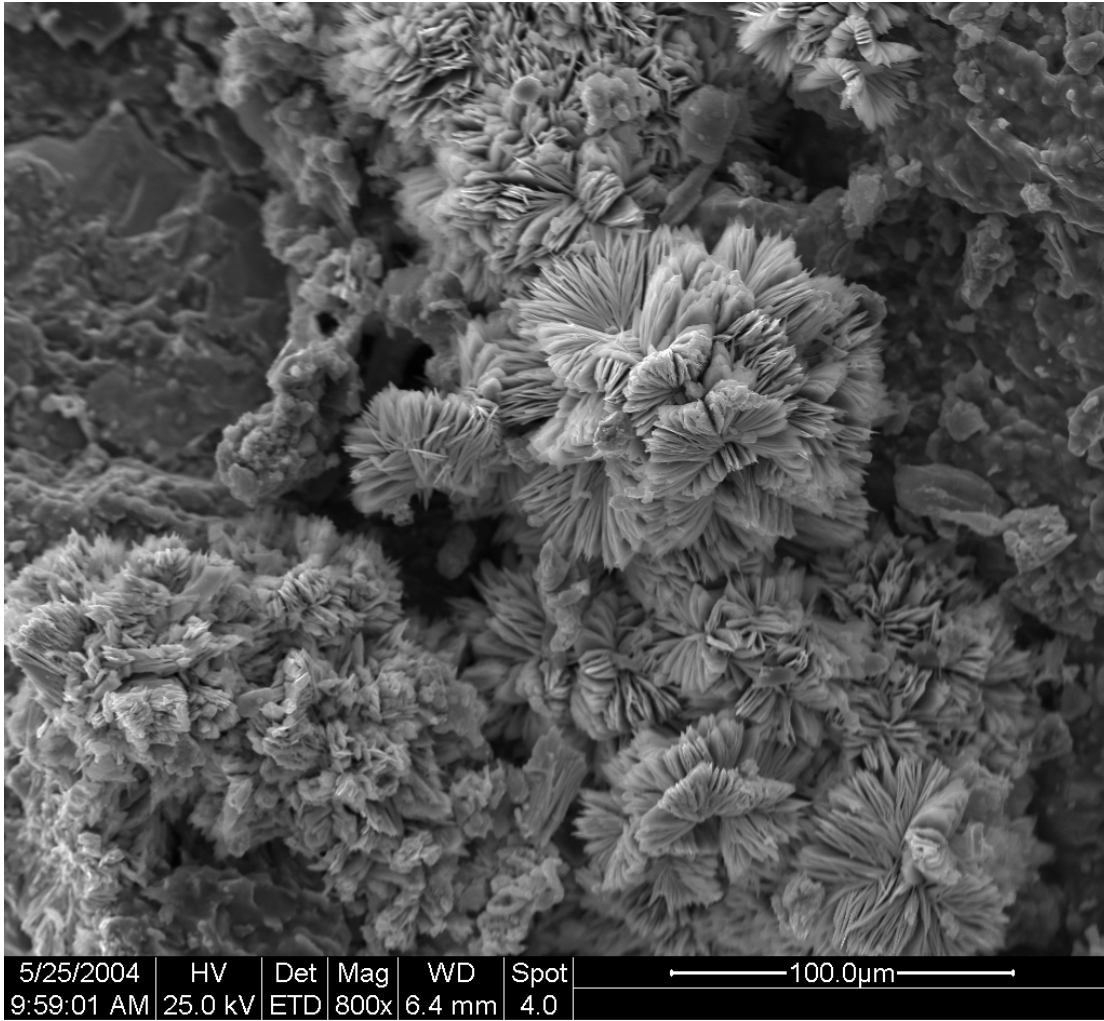


Figure 1c

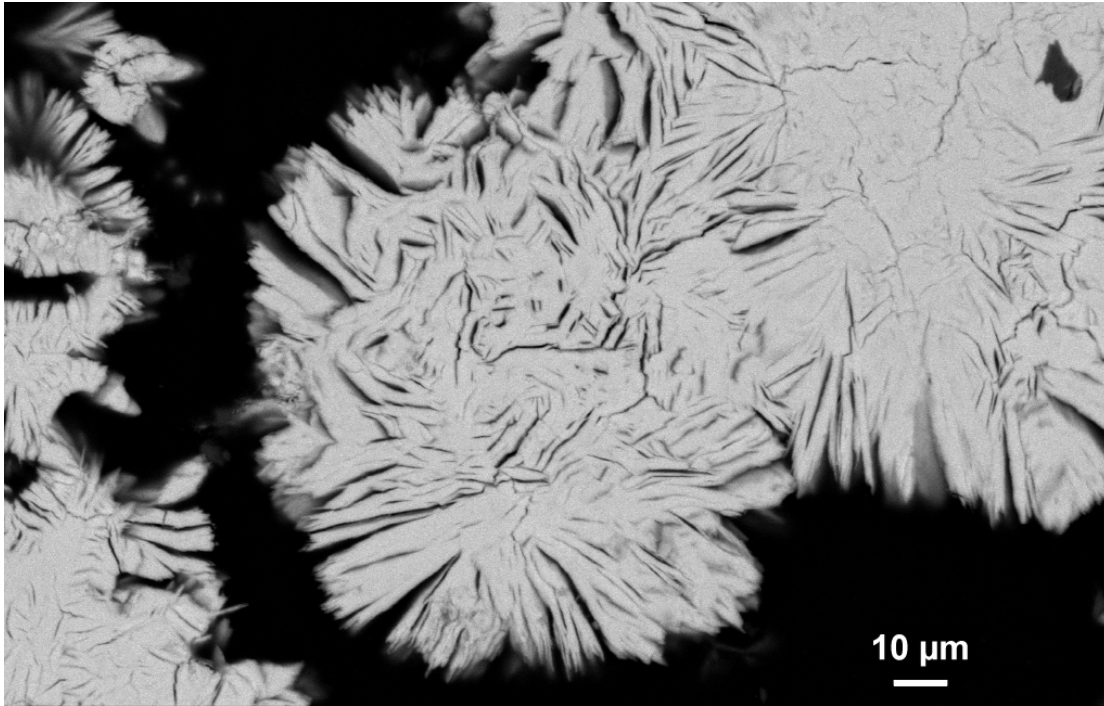


Figure 1d SEM back scattered image

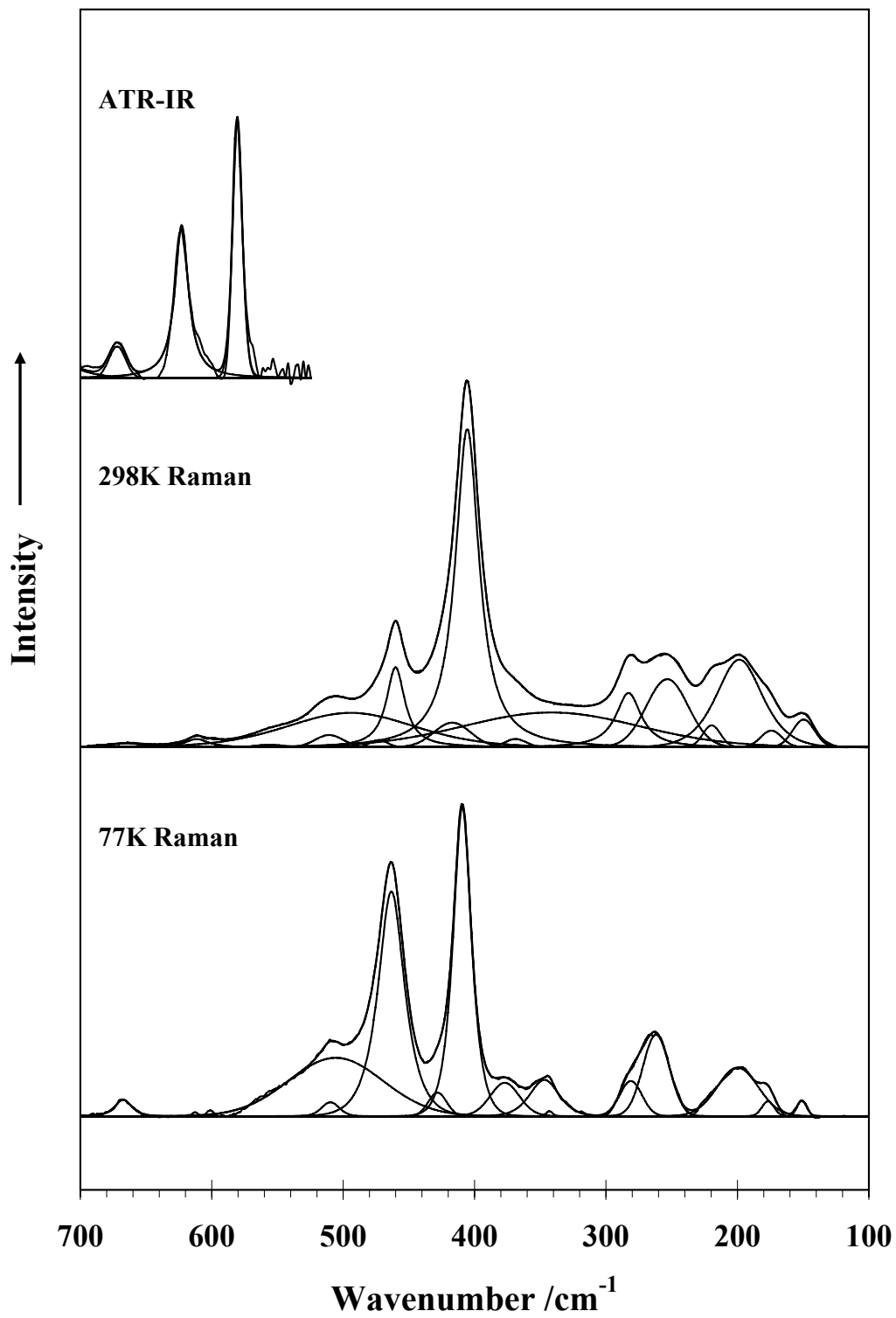


Figure 2

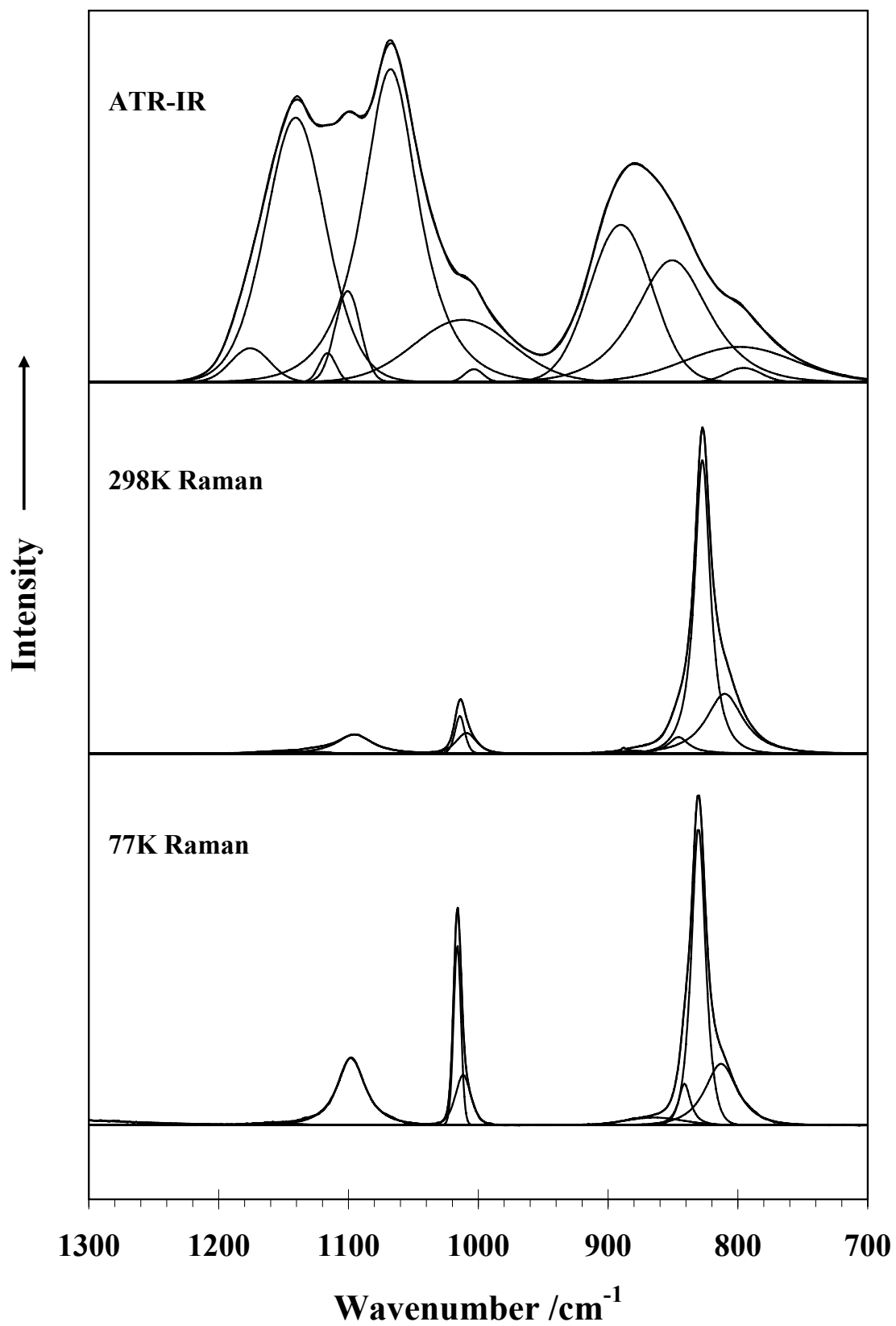


Figure 3

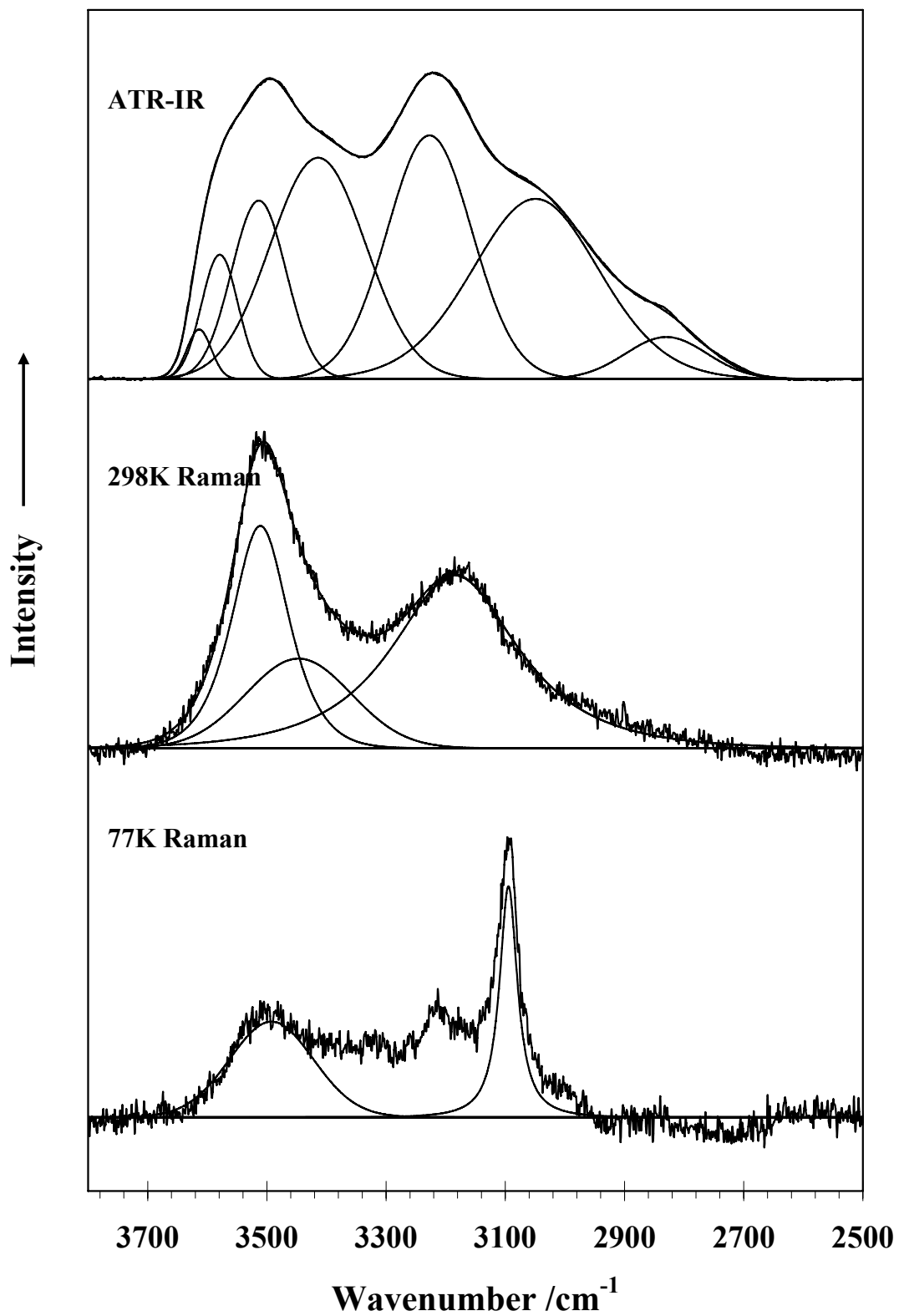


Figure 4

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