Raman and infrared spectroscopic studies of phurcalite from Red Canyon, Utah, USA – Implications for the molecular structure

Jiří Čejka [a,b], Jiří Sejkora [a], Ricardo Scholz [b], Andrés López [c], Yunfei Xi [c], Ray L. Frost [c,*]

[a] Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, CZ-193 00, Praha 9, Czech Republic
[b] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35, 400-00, Brazil
[c] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

HIGHLIGHTS

- Raman and infrared spectra of the uranyl mineral phurcalite $Ca_2(UO_2)_3O_2(PO_4)_2 \cdot 7H_2O$.
- From Red Canyon, Utah, USA.
- Observed bands were assigned to the stretching and bending vibrations of $(UO_2)^{2+}$ and $(PO_4)^{3-}$ units.
- Hydrogen bond lengths were inferred from observed stretching vibrations.
- Structurally nonequivalent U^{6+} and P^{5+} was inferred from the number of corresponding stretching bands.

GRAPHICAL ABSTRACT
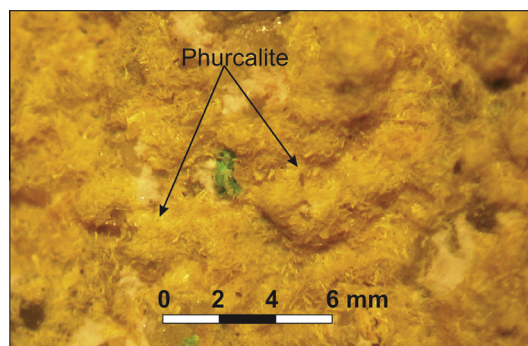
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ABSTRACT

Raman and infrared spectra of the uranyl mineral phurcalite, $Ca_2(UO_2)_3O_2(PO_4)_2 \cdot 7H_2O$, from Red Canyon, Utah, USA, were studied and tentatively interpreted. Observed bands were assigned to the stretching and bending vibrations of $(UO_2)^{2+}$ and $(PO_4)^{3-}$ units and to the stretching and bending vibrations and libration modes of water molecules. Approximate lengths of U–O in $(UO_2)^{2+}$ and O–H$\cdots$O hydrogen bond lengths were inferred from observed stretching vibrations. The presence of structurally nonequivalent U^{6+} and P^{5+} was inferred from the number of corresponding stretching bands of $(UO_2)^{2+}$ and $(PO_4)^{3-}$ units observed in the Raman and infrared spectra.

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Introduction

Uranium as a litophil element is characterised by strong affinity to oxygen, that neither an element, nor mineral sulphides, arsenides or halogenides have been found and all natural uranium compounds contain oxygen. The most important valences (oxidation numbers) under natural conditions are U^{4+} and U^{6+}.

U^{6+} forms the stable uranyl, $(UO_2)^{2+}$, ion. Uranyl ions participate in formation of uranyl minerals, such as uranyl oxide hydrates and uranates, silicates, phosphates, arsenates, vanadates, molybdates, sulphates, carbonates, selenites, tellurites and wolframates. Uranyl minerals are classified on the basis of their anions e.g. [1] or uranyl anion topology e.g. [2]. Some uranyl phosphates, uranyl arsenates, uranyl selenites, uranyl sulphates and uranyl carbonates contain sheets based upon anion topologies with triangles, squares, pentagons and hexagons [2,3]. The phosphuranylite sheet anion topology contains pentagons that share edges, resulting in dimers,

* Corresponding author. Tel.: +61 7 3864 2407; fax: +61 7 3864 1804.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

which are in turn linked into chains by sharing edges with hexagons. These chains are linked through chains of edge sharing triangles and squares, arranged such that the triangles and squares alternate along the chain (for details see especially [2,3], and may be also e.g. [4,5]). According to Locock [6], the minerals of the phosphuranylite group are hydrated phosphates and arsenates, with the general formula $A_k^{i+}[(UO_2)_3(XO_4)_2\Phi_2]\cdot nH_2O$, where A = monovalent, divalent, trivalent, or tetravalent cations (or complex cations), X = P^{5+}, or As^{5+}, and $\Phi = O^{2-}$ or $(OH)^-$. These minerals are defined by the presence of the phosphuranylite type sheet, which contains uranyl pentagonal and hexagonal bipyramids as coordination polyhedra, which share edges to form chains, and in turn are cross-linked by sharing vertices and edges with phosphates or arsenates tetrahedra. The interlayer region generally contains cations and water molecules, and the sheets are usually linked by hydrogen bonding and through bonds from the interlayer cations to oxygen atoms of the sheets. In some cases, sheets in minerals of the phosphuranylite group are linked by bonds to polyhedra of U^{6+} in the interlayer, resulting in framework structures [6].

Phurcalite was first described at Bergen an der Trieb, Saxony, Germany by Deliens and Piret [7] as $Ca_2(UO_2)_3(PO_4)_2(OH)_4\cdot 4H_2O$. Piret and Declerq determined crystal structure of phurcalite [8]. Phurcalite was also described at some other localities [9–19]. Redetermination of the crystal structure of phurcalite was carried out by Silva [20], Atencio [21] and Atencio et al. [15]. On this basis, chemical formula of phurcalite $Ca_2(UO_2)_3O_2(PO_4)_2\cdot 7H_2O$ was inferred. Infrared spectrum of phurcalite was published and partly interpreted by Camargo [9], Braithwaite et al. [18], and Atencio et al. [15]. Raman spectra of two phurcalite samples are available in the RRUFF data base, however, as usually, without any interpretation. Infrared and Raman spectra of phurcalite were presented also by Frost et al. [22].

Phurcalite, $Ca_2(UO_2)_3O_2(PO_4)_2\cdot 7H_2O$, is orthorhombic, space group $Pbca = D_{2h}^{15}$. The crystal structure of phurcalite consists of $[(UO_2)_3O_2(PO_4)_2]^{4n-}_n$, which are connected by Ca^{2+} cations and seven water molecules. In the crystal structure, there are three symmetrically (structurally) distinct (nonequivalent) U^{6+} coordination polyhedra, one hexaxonal bipyramid and two pentagonal bipyramids, two symmetrically different Ca^{2+} cations, one capped trigonal prism and one triangulated dodecahedron, and two structurally nonequivalent P^{5+} tetrahedra. Intersheet linkage is increased through hydrogen bonding from the water molecules to oxygen anions of the sheets [15].

Experimental

Mineral

The phurcalite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-136. The phurcalite sample originated from the Posey Mine, Red Canyon, White Canyon District, San Juan Co., Utah, USA. Carefull handpicked sample was used for X-ray powder diffraction experiment. To minimize the complicated shape of background, the samples studied were placed on a flat low-background silicon wafer. Powder XRD measurements were carried out with CuKα radiation at a Bruker D8 Advance diffractometer (40 kV, 40 mA) in the range 4-60° 2θ in the step-scan mode 0.01 /20 s. First, the mineral was semi-quantitatively analysed by EDS methods for chemical composition. Later, phurcalite was quantitatively analysed by Cameca SX 100 electron microprobe system in wavelength dispersion mode. Studied sample was mounted into the epoxide resin and polished. The polished surface was coated with carbon layer 250 Å. An acceleration voltage of 15 kV, a specimen current of 10 nA, and a beam

diameter of 5 μm were used. Well-defined natural and synthetic compounds were used as standards. The raw intensities were converted to the concentrations using automatic *PAP* matrix correction software package.

Raman spectroscopy

The crystals of phurcalite were placed on the stage of an Olympus BHSM microscope, equipped with 10× and 50× 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).

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).

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was 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 Gauss–Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.
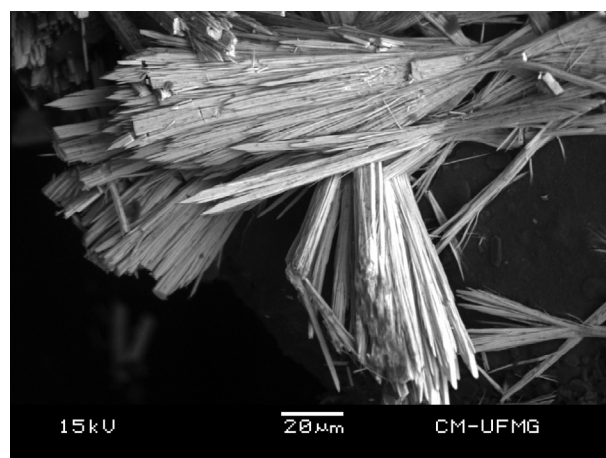

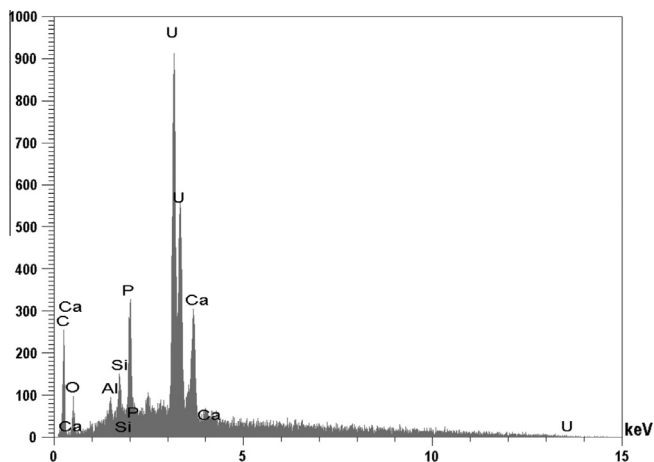**Fig. 1.** Backscattered electron image (BSI) of a phurcalite crystal aggregate up to 0.2 mm in length.

Fig. 2. EDS analysis of phurcalite.

Results and discussion

Characterization of studied sample

The BSI image of phurcalite sample studied in this work is shown in Fig. 1. The image shows a 200 μm aggregate of needle-like crystals. The unit-cell parameters of phurcalite refined from measured powder XRD: a 17.391(1), b 15.984(1), c 13.561(2) Å, V 3769.8(6) Å³, Z 8, agree very well with published data [15]. A semi-quantitative EDS analysis shows calcium uranyl phosphate with minor amounts of Si and Al (Fig. 2). The results of EPMA study

(mean of 13 point analyses) - CaO 8.51, SiO$_2$ 0.36 P$_2$O$_5$ 10.81, UO$_3$ 69.93, H$_2$O (calc.) 9.99, total 99.60 wt. % yield on the basis of 7 *apfu* to empirical formulae Ca$_{1.92}$(UO$_2$)$_{3.09}$[(PO$_4$)$_{1.92}$(SiO$_4$)$_{0.08}$]$_{\Sigma 2.00}$-O$_{1.97}$.7H$_2$O. Minor content of Al (ED spectrum) was not confirmed by EPMA data, it probably represents only a heterogeneous contamination of sample surface.

Raman and infrared spectroscopy

From the Raman and infrared spectra of phurcalite may be inferred the presence of uranyl ions, (UO$_2$)$^{2+}$, phosphate ions, (PO$_4$)$^{3-}$, and hydrogen bonded water molecules in its crystal structure. A free uranyl, (UO$_2$)$^{2+}$, point symmetry $D_{\infty h}$, should exhibit three fundamental modes: (a) symmetric stretching vibration v_1 ($\sum_g^+$), Raman active, approximately 900–750 cm^{-1}, (b) doubly degenerate bending vibration v_2 (δ) (Π_u), infrared active, approximately 300–200 cm^{-1}, and (c) antisymmetric stretching vibration v_3 (Σ_u), infrared active, approximately 100–850 cm^{-1} [23]. Tetrahedral *Td* symmetry is characteristic for phosphate, (PO$_4$)$^{3-}$, anions. In the case of a free ion, there are nine normal vibrations characterised by four fundamental distinguishable modes of vibrations: (a) symmetric stretching vibration v_1 (A_1), Raman active, approximately 990–930 cm^{-1}, (b) doubly degenerate in-plane bending vibration v_2 (δ) (E), Raman active, approximately 490–410 cm^{-1}, (c) triply degenerate antisymmetric stretching vibration v_3 (F_2), infrared and Raman active, approximately 1140–975 cm^{-1}, and (d) triply degenerate out-of-plane bending vibration v_4 (δ) (F_2), infrared and Raman active, approximately 670–510 cm^{-1} [23–28]. Molecular water, H$_2$O, (point symmetry C_{2v} is characterised by three fundamentals, symmetric and antisymmetric OH stretching
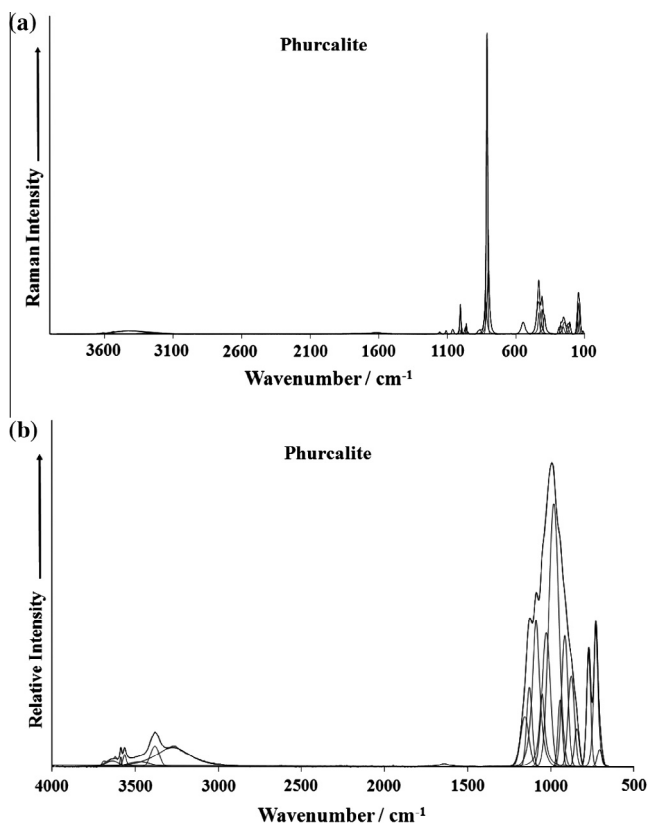

Fig. 3. (a) Raman spectrum of phurcalite (upper spectrum) over the 100–4000 cm^{-1} spectral range and (b) infrared spectrum of phurcalite (lower spectrum) over the 500–4000 cm^{-1} spectral range.
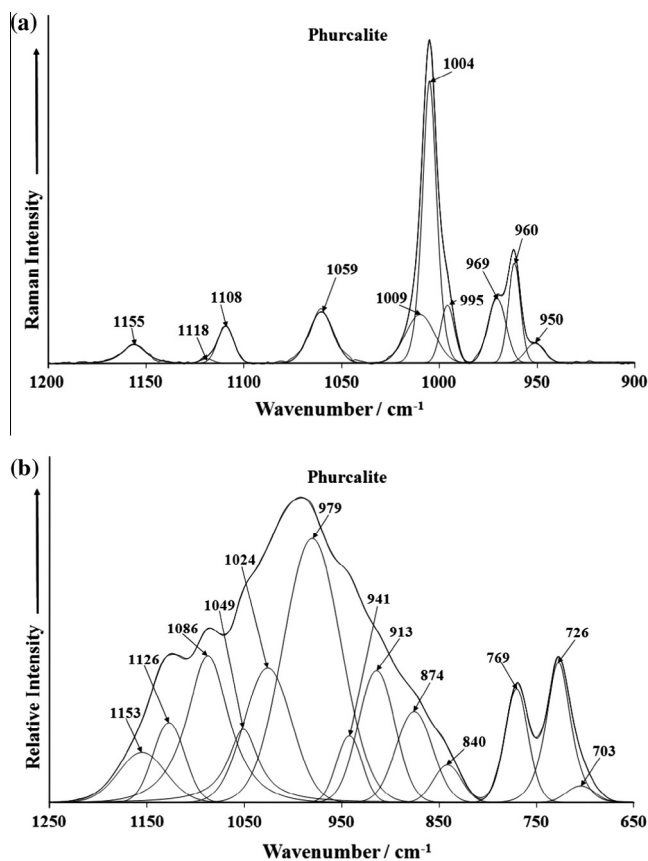
Fig. 4. (a) Raman spectrum of phurcalite (upper spectrum) in the 900–1200 cm^{-1} spectral range and (b) infrared spectrum of phurcalite (lower spectrum) in the 650–1250 cm^{-1} spectral range.
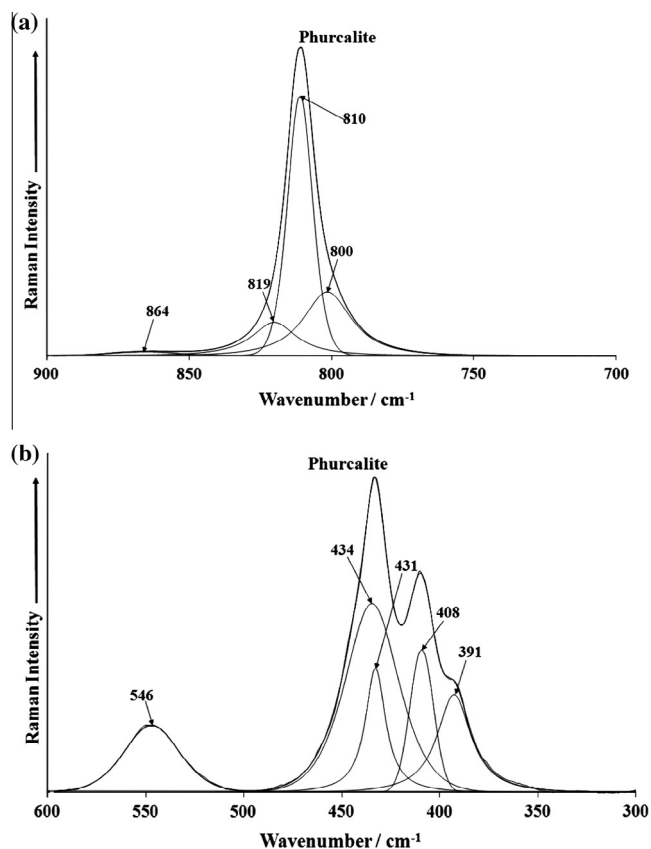
Fig. 5. (a) Raman spectrum of phurcalite (upper spectrum) in the 700–900 cm^{-1} spectral range and (b) Raman spectrum of phurcalite (lower spectrum) in the 300–600 cm^{-1} spectral range.
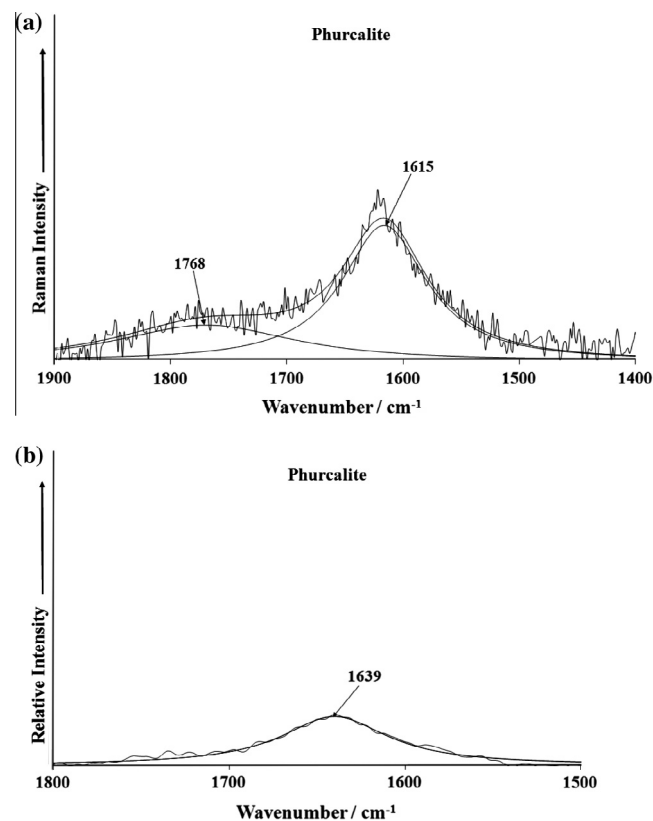

Fig. 6. (a) Raman spectrum of phurcalite (upper spectrum) in the 1400–1900 cm^{-1} spectral range and (b) infrared spectrum of phurcalite (lower spectrum) in the 1500–1800 cm^{-1} spectral range.

vibrations v_1 (A_1) (H$_2$O (g) 3656.65 cm^{-1}) and v_3 (B_1) (H$_2$O (g) 3755.79 cm^{-1}), both approximately 3600–2900 cm^{-1}, and bending vibration v_2 (δ H$_2$O) (A_1), approximately 1700–1590 cm^{-1}. All vibrations are infrared and Raman active. In the range of approximately 900–300 cm^{-1}, three types of libration modes can occur: τ-twisting, ω-wagging, and ρ-rocking [23,25]. Raman spectra of the phurcalite sample studied are presented in Figs. 3a (4000–100 cm^{-1}), 4a (1300–800 cm^{-1}), 5a (800–300 cm^{-1}), 5b (500–300 cm^{-1}), 6a (3800–3000 cm^{-1}) and 7a (1800–1300 cm^{-1}), its infrared spectra in Figs. 3b (4000–500 cm^{-1}), 4b (1300–500 cm^{-1}), 6b (3800–2600 cm^{-1}) and 7b (1800–1300 cm^{-1}).

Raman and infrared bands of uranyl, (UO$_2$)$^{2+}$, units

A Raman band at 810 cm^{-1} with two shoulders at 800 and 819 cm^{-1} is assigned to the v_1 (UO$_2$)$^{2+}$ symmetric stretching vibrations. Their number supports the X-ray single crystal structure analysis, from which was inferred that phurcalite contains three nonequivalent, structurally (symmetrically) different U^{6+} in its crystal structure. RRUFF samples R050534 and R060698 exhibit a Raman band approximately at 806 cm^{-1} with shoulders at 800 and 815 cm^{-1}, and 810 cm^{-1}, respectively. According to Bartlett and Cooney [26], U–O bond lengths in uranyl, (UO$_2$)$^{2+}$, may be inferred from the wavenumbers assigned to the v_1 (UO$_2$)$^{2+}$. For 810 cm^{-1} (this paper), this calculated value is 1.80 Å, for RRUFF samples ~809 cm^{-1} and 1.802 Å. These values are in excellent agreement with ∅ 1.805 (1.81; 1.179; 1.815) Å inferred from the X-ray single crystal structure analysis [15]. Wavenumbers of Raman bands of the samples studied by Frost et al. [22] which may be attributed to the v_1 (UO$_2$)$^{2+}$ vary approximately from 796 to

811 cm^{-1}, and therefore approximately from 1.81 to 1.80 Å. Wavenumbers of the infrared bands attributed to the v_3 (UO$_2$)$^{2+}$ antisymmetric stretching vibrations are 874 cm^{-1} (this paper), 893 or 884 cm^{-1} (two samples) [9], 890 cm^{-1} [18], 885 cm^{-1} [15] and approximately from 861 to 888 cm^{-1} [22]. Calculated values are 1.804, 1.79, 1.804, 1.79, 1.796, 1.814 to 1.793 Å, respectively, the average of them is ~1.80 Å. Also all these calculated U–O bond lengths in uranyl of the sample studied in this paper and those published are close to the lengths for three structurally nonequivalent uranyls given from the X-ray single crystal structure analysis of phurcalite by Atencio et al. [15]. Raman spectra below 300 cm^{-1} were not recorded. However, from the RRUFF data base and also [22] may be inferred that Raman bands related to the v_2 (δ) bending vibrations are located close to 250 cm^{-1}. Corresponding infrared band was observed at 255 cm^{-1} [15]. U–O bond lengths in uranyls, inferred from the wavenumbers of Raman and infrared bands assigned to uranyl stretching vibrations, are in agreement with the data presented by Burns [2,27].

Raman and infrared bands of phosphate, (PO$_4$)$^{3-}$, units

Raman bands at 1155, 1118, 1108, 1059, 1009, 1004 cm^{-1} and infrared bands at 1153, 1126, 1086, 1049 and 1024 cm^{-1} are assigned to the split triply degenerate v_3 (PO$_4$)$^{3-}$ antisymmetric stretching vibrations. Camargo [9] observed infrared bands at 1151, 1106, 1052 and 1000; 1136, 1098, 1042 cm^{-1} (two samples were studied), Brathwaite et al. [18] at 1148, 1110, 1063 and 1000; 1150, 1105, 1070 cm^{-1} (two samples were studied), Atencio et al. [15] two bands at 1140 and 1055 cm^{-1}, and Frost et al. [22] infrared bands at 1148, 1110, 1080, 1052 and 1024, 1150, 1127, 1110,
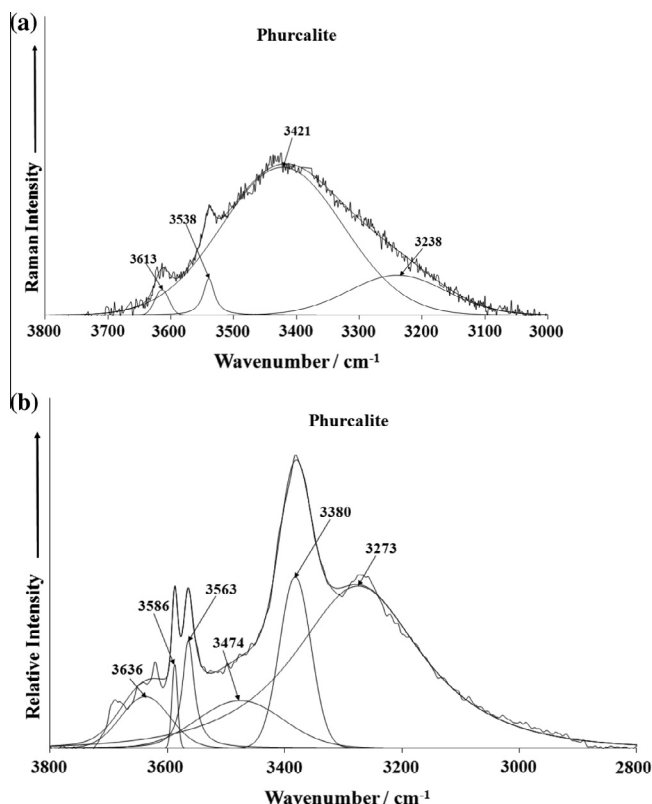
Fig. 7. (a) Raman spectrum of phurcalite (upper spectrum) in the 3000–3800 cm^{-1} spectral range and (b) infrared spectrum of phurcalite (lower spectrum) in the 2800–3800 cm^{-1} spectral range.

1062 and 1027; 1146, 1127, 1106, 1085, 1059 and 1029 cm^{-1} and Raman bands at 1105 and 1051; 1156, 1104, 1055 and 1007; 1151, and 1104 cm^{-1} (three samples were studied).

Raman bands at 995, 969, 960 and 950 cm^{-1} and infrared bands at 979 and 941 cm^{-1} are attributed to the v_1 (PO$_4$)$^{3-}$ symmetric stretching vibrations. Braithwaite et al. [18] observed infrared bands at 970 and 970 cm^{-1} (two samples studied), Atencio et al. [15] an infrared band at 960 cm^{-1}, and Frost et al. [22] Raman bands at 997 and 956, 992, 967 and 958; 998 and 967 cm^{-1} (three samples studied).

The number of the observed bands proves the presence of structurally (symmetrically) nonequivalent phosphate units in the crystal structure of phurcalite. This is in agreement with the single crystal structure analysis of phurcalite.

A Raman band at 546 cm^{-1} and Raman bands at 434, 431, 408 and 391 cm^{-1} are assigned to the triply degenerate v_4 (δ) (PO$_4$)$^{3-}$ out-of-plane bending vibration and to the doubly degenerate v_2 (δ) (PO$_4$)$^{3-}$ in plane bending vibrations, respectively. Braithwaite et al. [18] observed an infrared broad band at (590) cm^{-1} and another infrared band at 545 cm^{-1}, in the second sample, only once band at 540 cm^{-1} was observed. Atencio et al. [15] described corresponding infrared bands at 575 and 540 cm^{-1} and 385 and 255 cm^{-1}, respectively.

Raman and infrared bands of molecular water vibrations

Raman bands at 3613, 3538, 3421 and 3238 cm^{-1} and infrared bands at 3636, 3586, 3563, 3474, 3380 and 3238 cm^{-1} are assigned to the v OH stretching vibrations of structurally distinct and differ-

ently hydrogen bonded water molecules. According to Libowitzky [28], O–H$\cdots$O hydrogen bond lengths approximately vary in the range from free or very weakly hydrogen bond hydrogen bonded water molecules (>3.2 Å) to relatively strong hydrogen bonded water molecules ($\sim$2.72 Å). Camargo studied to samples of his mineral X (in fact phurcalite) [9] and observed infrared bands at 3423 and 3335 cm^{-1}, respectively, Braihwaite et al. [18] a broad band at 3400 cm^{-1} and a band at 3180 cm^{-1}, Atentio et al. [15] a broad band at 3400 cm^{-1}, Frost et al. [22] on studying three phurcalite samples up to twelve infrared bands between 3700 and 2700 cm^{-1}.

A Raman at 1615 cm^{-1} and a broad infrared band at 1639 cm^{-1} are assigned to the v_2 (δ) H$_2$O bending vibrations. These values correspond with infrared bands at 1612 or 1585 cm^{-1} [9], a broad infrared band at 1625 cm^{-1} [18], an infrared band at 1615 cm^{-1} [15], and three infrared bands approximately in the range from 1678 to 1594 cm^{-1} observed in three samples studied by Frost et al. [22]. Infrared bands at 941, 913, 769, 726 and 703 cm^{-1} may probably be related to the libration modes of hydrogen bonded water molecules. Only Frost et al. [22] observed infrared bands in these regions.

Conclusions

(a) Raman and infrared spectra of phurcalite from Red Canyon, Utah, USA, were recorded and tentatively interpreted.

(b) Observed Raman and infrared bands were tentatively assigned to the stretching and bending vibrations of (UO$_2$)$^{2+}$ and (PO$_2$)$^{3-}$ units and water molecules.

(c) Approximate U–O bond lengths in uranyl were calculated from the wavenumbers of the (UO$_2$)$^{2+}$ symmetric and anti-symmetric stretching vibrations [26]. These values are in agreement with the data of the crystal structure analysis of phurcalite [15] and general data presented by Burns [2,27].

(d) Approximate O–H$\cdots$O hydrogen bond lengths of water molecules were inferred from the wavenumbers of the v OH stretching vibrations of water molecules [28].

(e) The presence of symmetrically nonequivalent (UO$_2$)$^{2+}$ and (PO$_4$)$^{3-}$ and water molecules in the crystal structure of phurcalite was inferred from the observed number of these structural units. This agrees with the data from X-ray single crystal structure analysis [15].

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