THE STRUCTURE AND PHYSICOCHEMICAL CHARACTERISTICS OF SYNTHETIC ZIPPEITE

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Abstract

Zippeite was synthezised by adjusting a UO_2SO_4 solution containing K_2SO_4 to a pH of 3.6 by means of KOH and keeping it for 75 hours at 150°C and an approximate pressure of 3.5 MPa. The crystals are yellow and well-formed. Chemical analysis gives $K(UO_2)_2(SO_4)(OH)_3 \cdot H_2O$ as the composition. The strongest lines of the X-ray pattern correspond to d values of 7.06, 3.51, 3.14, 2.86, and 2.65 Å. The pattern is identical to the pattern of natural zippeite. Single-crystal X-ray studies revealed the composition $K(UO_2)_2SO_4(OH)_3 \cdot H_2O$. The crystals are monoclinic, space group $C2/c$, with a 8.755(3), b 13.987(7), c 17.730(7) Å, β 104.13(3)°, and $Z = 8$. The density D_m is 4.8, and D_x is 4.7 g/cm^3. The crystal structure was solved by Patterson methods. The structure has been refined to an unweighted residual of 0.053. Zippeite possesses a layer structure parallel to (010). $UO_4(OH)_3$ pentagonal bipyramids are the building blocks of a unique pattern of double polyhedra linked along the a axis by edge-sharing of OH-groups. The $UO_4(OH)_3$ chains are joined by chains of SO_4 polyhedra into infinite $(UO_2)_2(OH)_2SO_4$ sheets. Two $(UO_2)_2(OH)_2SO_4$ sheets sandwich planar layers of K$^+$, OH$^-$, and H_2O at $y \approx$ ¼ and ¾. The crystals show a moderate fluorescence between 520 and 620 nm, with unresolved bands at room temperature, but with three distinct bands at 77 K. The infrared spectrum was recorded, and the most important bands were assigned. The optical parameters were determined. The crystals have a moderate solubility, with the solubility product found to be $10^{-42.60}$.

Keywords: zippeite, synthesis, crystal structure, physicochemical properties.

Sommaire

Nous avons réussi à synthétiser la zippéite en ajustant le pH d'une solution UO_2SO_4 contenant K_2SO_4 à 3.6 en y ajoutant KOH et en la laissant pour 75 heures à 150°C et environ 3.5 MPa. Les cristaux sont jaunes et bien formés. Une analyse chimique a donné $K(UO_2)_2(SO_4)(OH)_3 \cdot H_2O$. Les raies les plus intenses du spectre de diffraction sont situés à une valeur d de 7.06, 3.51, 3.14, 2.86 et 2.65 Å. Ce spectre est identique à celui de la zippéite naturelle. Des études sur cristal unique par diffraction X confirment la composition, et montrent que la zippéite est monoclinique, groupe spatial $C2/c$, avec a 8.755(3), b 13.987(7), c 17.730(7) Å, β 104.13(3)°, $Z = 8$. La densité mesurée D_m est 4.8, et la densité calculée D_x est 4.7 g/cm^3. Nous avons résolu la structure par méthodes de Patterson jusqu'à un résidu R de 0.053. La zippéite est faite de couches parallèles à (010). Des pentagones bipyramidaux $UO_4(OH)_3$ sont l'unité structurale de base d'un agencement unique de polyèdres doubles alignés le long de l'axe a par partage d'arêtes impliquant des groupes OH. Les chaînes $UO_4(OH)_3$ sont liées par des chaînes de polyèdres SO_4 pour former des feuillets de stoechiométrie $(UO_2)_2(OH)_2SO_4$. Entre deux de ces feuillets se trouvent des couches de K$^+$, OH$^-$ et H_2O à une élévation y d'environ ¼ et ¾. Les cristaux montrent une fluorescence moyenne entre 520 et 620 nm, avec des bandes non résolues à température ambiante, et trois bandes distinctes à 77 K. Nous avons mesuré et interprété le spectre infrarouge, et nous avons déterminé les propriétés optiques. Les cristaux sont modérément solubles, et le produit de solubilité est $10^{-42.60}$.

(Traduit par la Rédaction)

Mots-clés: zippéite, synthèse, structure cristalline, propriétés physicochimiques.

INTRODUCTION

Zippeite is a secondary uranium-bearing mineral belonging to the group of basic uranyl sulfates. This mineral is of recent formation and occurs as a yellow earthy efflorescence and glassy crust on the walls of mine workings containing uraninite. The mineral has a hardness of about 2 and is easily soluble in acids. Its formation results from the oxidation reaction of uraninite in a H_2SO_4 medium, which in turn is formed by the oxidation of metal sulfides in a relatively humid atmosphere.

Zippeite is most commonly associated with gypsum and uranopilite $[(UO_2)_6(SO_4)(OH)_{10} \cdot 12H_2O]$, and less commonly with johannite $[Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 8H_2O]$ and uranophane $[Ca(H_3O)_2[(UO_2)_2(SiO_4)_2] \cdot 3H_2O]$. Numerous localities are described in the literature (Frondel 1958). There is some confusion concerning its composition, structure, and related properties. Nováček (1935) described the mineral as $2UO_3 \cdot SO_3 \cdot nH_2O$, with n being 5 or 6, whereas Hess (1924) proposed the formula $2UO_3 \cdot SO_3 \cdot 3H_2O$. Traill (1952) described a synthetic zippeite phase as a basic uranyl sulfate $(UO_2)_2SO_4(OH)_2 \cdot 4H_2O$, and Frondel (1958) proposed the formula $2UO_3 \cdot SO_3 \cdot 5H_2O$. More recently, Frondel et al. (1976) found, on the basis of accurate chemical analytical data, that the structure of zippeite contains potassium, and proposed that zippeite is a K-bearing basic uranyl sulfate with the formula $K_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$.

As natural zippeite is not suitable for single-crystal studies, the aim of our research was to synthesize zippeite under moderate pressure and temperature, and to use the resulting well-formed crystals for a determination of its structure. This synthetic zippeite is further characterized by its infrared and luminescence spectra, its solubility product, and optical parameters.

SYNTHESIS

In order to synthesize a sufficient quantity of zippeite, several experiments were necessary. A 50 mL solution of 0.075 M UO_2SO_4 was mixed with 1.5 g of K_2SO_4 and adjusted to a pH of 3.6 by means of KOH. This solution was introduced into a 170 mL teflon-lined bomb, resulting in a 30% degree of filling. The bomb was heated for 75 hours at 150°C, which resulted in an approximate pressure of 3.5 MPa. The crystals obtained were washed several times with distilled water and subsequently air-dried. They were large enough and sufficiently well-formed for a single-crystal study. A scanning electron micrograph (Fig. 1) shows that the crystals are monoclinic, with a plate-like habit and truncated edges. The height of the crystals ranges from 0.1 to 0.25 mm, and the width ranges from 0.05 to 0.1 mm. The SEM photograph in Figure 1 shows that the morphology of the crystals can be considered as a combination of the forms {101} and {010} and two domes.

CHEMICAL COMPOSITION

The air-dried synthetic compound was dissolved in 6 M HCl. The K_2O content of the resulting solution was determined by atomic absorption spectrophotometry using a Philips Pye Unicam model PU 9200 atomic absorption spectrophotometer. The UO_3 content was also determined spectrophotometrically by means of a Pye Unicam SP8–100 ultraviolet spectrophotometer using arsenazo III as the reagent, the optical
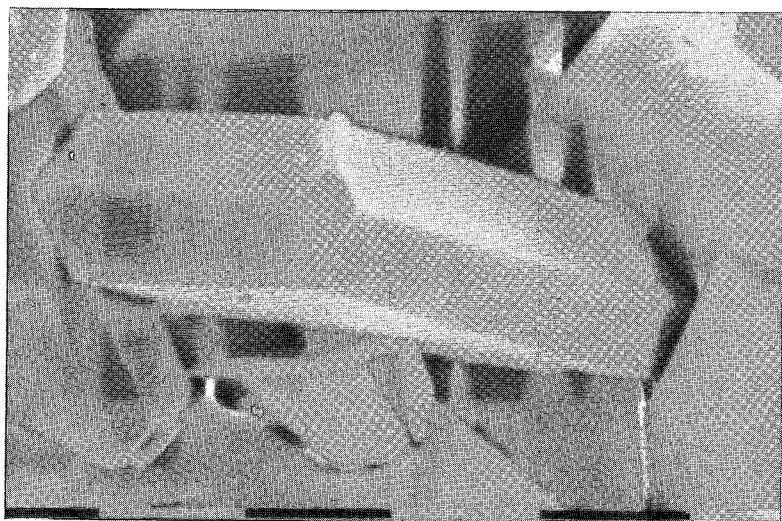

Fig. 1. Scanning electron micrograph of the synthetic crystals. The size bar is divided into 10 μm units.

TABLE 1. CHEMICAL COMPOSITION OF SYNTHETIC ZIPPEITE

Oxide	weight %	Atomic quantities (x 10^4)	Atomic ratio
K_2O	7.56	802.5	1.13
UO_3	75.90	2653	1.88
SO_3	10.63	1327	0.94
H_2O	6.17	-	-
Total	100.51		

$K_{1.13}(UO_2)_{1.88}(SO_4)_{0.94}(OH)_3 \cdot 0.88H_2O$

density being measured at 662.5 nm (Singer & Matucha 1962). The SO_3 content was determined gravimetrically as $BaSO_4$. The water content was determined by thermogravimetric analysis, which will be discussed separately. Table 1 summarizes the results of the chemical analysis and the computed atomic ratios.

From the oxide composition, the chemical formula was calculated by the classical residual oxygen method based on 11 atoms of oxygen, the result being: $K_{1.13}(UO_2)_{1.88}(SO_4)_{0.94}(OH)_3 \cdot 0.88H_2O$ or, ideally, $K(UO_2)_2SO_4(OH)_3 \cdot H_2O$. The crystal-structure analysis showed that $Z = 8$.

The thermal stability of the synthetic crystals was investigated by thermogravimetry (TG) combined with differential scanning calorimetry (DSC). A Dupont DSC 910 and TGA 951 apparatus was used with an applied heating rate of 5°C/min and a N_2 flow of 30 mL/min. The TG curve and its derivative are represented in Figures 2A and 2B, respectively.
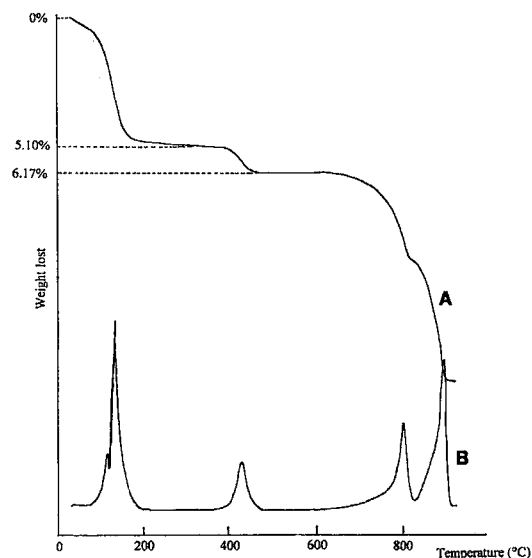

FIG. 2. Thermogravimetric (A) and differential thermogravimetric (B) curves of the synthetic crystals.

From the TG curves, a total loss of 6.17% H_2O was deduced. In the range 30° – 150°C, 1.97 molecules of H_2O were lost, whereas between 150° and 450°C, 0.41 molecules of water were lost. The total number of water molecules lost over the whole range is therefore 2.38. The loss of SO_3 takes place in the region 650° – 900°C.

X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction data were recorded at 40 kV and 20 mA using CuKα₁ radiation (λ = 1.5406 Å) and a Guinier–Hägg camera with a diameter of 100 mm. Silicon powder (NBS–640) was used as a calibration standard. The relative intensities of the diffraction lines were measured with a Carl Zeiss Jena MD–100 microdensitometer. The results are given in Table 2. The X-ray pattern of the synthetic material is identical with the data given by Traill (1952) (JCPDS 8–138) and Frondel (1958) (JCPDS 29–1062), so the compound can be identified definitively as synthetic zippeite.

STRUCTURE DETERMINATION

Many crystals are twinned. Crystals suitable for diffraction work were sought by microscopic examination under polarized light. Only crystals that extinguish uniformly were selected. Crystal quality was further assessed by noting the quality of X-ray-diffraction spots on Weissenberg films. Appropriate peak-shape and width on diffractograms revealed that the selected crystals are untwinned and have good crystallinity. Weissenberg photographs showed a monoclinic C-centered lattice (systematic absences for $h + k = 2n + 1$ for all reflections, and $l = 2n + 1$ for $h0l$ reflections). An orthorhombic pseudocell with the same dimensions as the unit cell was described by Frondel et al. (1976), but the very weak superstructure diffraction-maxima (requiring doubling of the orthorhombic b-axis) could not be detected either with an overexposed (200 h) Weissenberg photograph or with a four-circle diffractometer. An orthorhombic space-group that fits the observed intensities could not be found.

A transparent, yellow, plate-like crystal was mounted on a single-crystal diffractometer. Unit-cell dimensions and an orientation matrix for data measurement were obtained from a least-squares refinement using the setting angles of 24 centered reflections in the range $19 < 2\theta < 25°$. Accurate cell parameters were obtained by least-squares refinement of measured and calculated $(\sin \theta)^2$-values of 24 reflections (Stoe 1988a). Two reflections were selected and used as intensity standards to monitor the measurements at 1-hour intervals. The intensity of the standard peaks varied ≤3% during data collection (13 days). The intensity data were corrected for Lorentz-polarization

TABLE 2. X–RAY POWDER–DIFFRACTION DATA: SYNTHETIC ZIPPEITE

Table 2. (continued)

d_{calc}	I_{calc}	h k l	2θ	d_{meas}	I_{meas}	d_{pub}*
8.597	19	0 0 2	10.28	8.590	12	8.58
7.251	3	-1 1 1	12.20	7.280	5	
6.993	100	0 2 0	12.65	7.000	100	6.95
6.237	1	1 1 1	14.19	6.250	2	6.24
5.425	11	0 2 2	16.33	5.428	5	5.41
4.298	7	0 0 4	20.65	4.290	21	4.29
4.245	4	2 0 0	20.91			
4.239	4	-2 0 2	20.94			4.24
3.875	5	1 3 1	22.93	3.890	3	3.85
3.662	5	0 2 4	24.29	3.660	19	
3.629	6	2 2 0	24.51			3.62
3.625	6	-2 2 2	24.54			
3.529	1	-1 3 3	25.21			
3.497	20	0 4 0	25.45	3.509	6	3.482
3.484	18	2 0 2	25.55	3.494	20	
3.474	17	-2 0 4	25.62	3.478	19	
3.239	3	0 4 2	27.52	3.232	4	3.227
3.118	33	2 2 2	28.60	3.120	42	3.108
3.111	33	-2 2 4	28.67	3.115	36	
2.8656	14	0 0 6	31.19	2.857	23	2.860
2.7981	1	-1 3 5	31.96	2.803	6	
2.7125	3	0 4 4	33.00	2.722	3	2.698
2.7080	1	2 0 4	33.05			
2.7004	1	-2 0 6	33.15			
2.6990	1	2 4 0	33.17			
2.6975	1	-2 4 2	33.18			
2.6565	1	-1 5 1	33.71	2.650	18	2.644
2.6516	14	0 2 6	33.78			
2.5959	3	1 5 1	34.52			2.592
2.5253	1	2 2 4	35.52			
2.4839	1	-1 5 3	36.13	2.484	6	
2.4680	6	2 4 2	36.37			2.460
2.4645	7	-2 4 4	36.43			
2.3311	3	0 6 0	38.59			2.321
2.2499	2	0 6 2	40.04			2.239
2.2237	1	-1 3 7	40.53			
2.2164	9	0 4 6	40.67	2.210	7	2.210
2.2072	1	-3 3 5	40.85	2.204	15	
2.1888	7	-4 0 2	41.21			2.189
2.1847	1	-1 5 5	41.29			
2.1492	1	0 0 8	42.01			
2.1448	2	2 0 6	42.10	2.144	5	2.140
2.1394	2	-2 0 8	42.21	2.138	5	
2.1227	1	4 0 0	42.56			
2.1197	1	-4 0 4	42.62	2.110	2	
2.0889	6	-4 2 2	43.28	2.090	9	2.089
2.0789	1	3 3 3	43.50	2.080	1	
2.0544	1	0 2 8	44.04	2.052	7	2.041
2.0505	3	2 2 6	44.13			
2.0492	1	0 6 4	44.16			
2.0458	3	-2 2 8	44.24			
2.0433	1	2 6 0	44.29			
2.0427	1	-2 6 2	44.31			
2.0311	2	4 2 0	44.57			
2.0285	1	-4 2 4	44.63			
2.0039	1	1 3 7	45.21			
1.9882	1	-3 5 3	45.59			
1.9528	1	4 0 2	46.46	1.960	3	
1.9482	1	-4 0 6	46.58	1.946	3	
1.9374	5	2 6 2	46.86	1.930	3	
1.9357	6	-2 6 4	46.90			1.932
1.9207	3	1 7 1	47.29			
1.8809	1	4 2 2	48.35	1.873	2	
1.8767	1	-4 2 6	48.47	1.860	2	
1.8740	1	-1 7 3	48.54			
1.8553	6	-4 4 2	49.06	1.851	4	1.855
1.8282	1	2 4 6	49.84			
1.8249	1	-2 4 8	49.93	1.820	1	
1.8145	1	4 4 0	50.24			
1.8083	4	0 6 6	50.42	1.800	1	
1.7869	2	3 5 3	51.07			1.797
1.7528	2	2 0 8	52.14	1.753	18	1.752
1.7491	2	-2 0 10	52.26			
1.7483	2	0 8 0	52.28	1.745	14	1.741
1.7419	3	4 0 4	52.49			
1.7386	1	1 5 7	52.60	1.732	3	
1.7370	3	-4 0 8	52.65			
1.7350	2	-1 7 5	52.72			
1.7194	1	0 0 10	53.23	1.714	4	
1.7133	1	0 8 2	53.44			
1.7019	1	-4 4 6	53.82			
1.7002	4	2 2 8	53.88	1.702	16	
1.6968	4	-2 2 10	54.00	1.694	10	1.697
1.6903	4	4 2 4	54.22			
1.6858	4	-4 2 8	54.38			1.687
1.6696	2	0 2 10	54.95	1.670	3	
1.6315	1	-3 7 3	56.35	1.649	1	
1.5957	2	-4 6 2	57.73			
1.5670	3	2 4 8	58.89			
1.5643	3	-2 4 10	59.00	1.564	4	
1.5626	1	2 8 2	59.07			
1.5617	1	-2 8 4	59.11			
1.5592	3	4 4 4	59.21	1.559	3	
1.5556	3	-4 4 8	59.36			
1.5168	2	1 9 1	61.04			
1.5147	1	3 7 3	61.13			

* Frondel et al. (1976)

(Stoe 1988b), and absorption effects (Stoe 1988c), the latter using ψ scans. The experimental conditions for data measurement, together with selected data about the crystal, are listed in Table 3. The structure was solved by Patterson methods using SHELXS (Sheldrick 1986). Fourier map and structure-factor calculation recycling methods were then used to locate the position of the other atoms in the asymmetric unit. The K position is divided into two half-occupied positions K1 and K2, which represent two closely spaced alternative positions for the same atom. They refined in a satisfactory manner, although their displacement factors are relatively large. The electron density of the hydrogen atoms was within the statistical background level, and thus no attempt was made to locate these atoms. The structure-factor calculations were carried out with the program SHELXL93 (Sheldrick 1993) using neutral-atom scattering factors and anomalous-dispersion corrections. The structure was refined with rigid bond and approximate isotropicity constraints (DELU, ISOR in SHELX93, respectively) for all atoms and appropriate distance-restraints for the sulfate and uranyl groups. The final unweighted R factor was 0.0531, and the results of the refinement are included in Table 3. Voids calculated in the residual structure with the program PLATON (Spek 1990) show a cavity of 19 Å^3 at the position of the highest positive difference-Fourier peak, a value that is smaller than the expected volume (40 Å^3) for a water molecule.

The crystal structure was also refined in the non-centrosymmetric space-group Cc, resulting in a higher R value, 0.066. This confirmed the choice of C2/c, which was made on the basis of the intensity statistics.

General calculations were performed using PARST (Nardelli 1983). The lists of structure factors and anisotropic displacement parameters have been deposited with the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Table 4 contains the refined positional and equivalent isotropic temperature-factors. The structure and numbering scheme of atoms are illustrated in the PLUTON (Spek 1992) plots shown in Figures 3 and 4.

CRYSTAL DATA

Crystal size (mm)	0.12 × 0.076 × 0.038
a (Å)	8.755(3)
b (Å)	13.987(7)
c (Å)	17.730(7)
ß (°)	104.13(3)
V (Å^3)	2105(2)
Formula weight	744.26
$F(000)$	2560
Space group	$C2/c$
Z	8
Formula	$O_{12}H_5K_1S_1U_2$
D_c (g/cm^3)	4.696
D_x (g/cm^3)	4.8
μ mm^{-1}	31.38

INTENSITY MEASUREMENT

Diffractometer	Stoe STADI4
Monochromator	graphite
Radiation	Mo$K\alpha$ (λ = 0.71069 Å)
Scan type	$\tilde{\omega}$–scan
2θ–range (°)	2.0 – 50.1
hkl ranges	$-10 \leq h \leq 10$
	$-16 \leq k \leq 16$
	$-21 \leq l \leq 21$
Number of reflections measured	14876
Number of unique reflections	1866
R_{int}	6.02
Number of reflections with $I > 3\sigma(I)$	502
T_{min} and T_{max} (transmission)	0.047 and 0.134

REFINEMENT OF THE STRUCTURE

Refinement on F^2, $w = 1/[\sigma^2(F_o^2) + 0.0865\ P]$; $P = (F_o^2 + 2\ F_c^2)/3$

Final R	0.0531
S (Goodness of Fit)	1.3 (156 parameters)
(Δ/σ)max	< 0.1 (mean = 0.002)
$\Delta\rho_{max}$ (eÅ^{-3})	2.3
$\Delta\rho_{min}$ (eÅ^{-3})	–5.1
extinction coefficient x	0.00030(1)
$F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]-1/4$	

Label	Occupancy	x/a	y/b	z/c	U_{eq}*
U1	1.0	0.1668(1)	0.01573(5)	0.08649(4)	0.0134(2)
U2	1.0	0.6665(1)	–0.01573(5)	0.08618(5)	0.0151(2)
S1	0.5	0.50000(0)	–0.0078(4)	0.25000(0)	0.0141(9)
S2	0.5	0.00000(0)	0.0016(4)	0.25000(0)	0.013(1)
O1	1.0	0.192(2)	0.1418(9)	0.0712(7)	0.0152(7)
O1'	1.0	0.198(2)	–0.1022(8)	0.1163(8)	0.014(1)
O2	1.0	0.651(2)	0.1072(8)	0.1110(8)	0.0160(8)
O2'	1.0	0.648(2)	–0.1353(8)	0.0557(8)	0.014(1)
O3	1.0	0.393(2)	–0.028(1)	0.0459(7)	0.0157(7)
O4	1.0	–0.099(2)	–0.0059(9)	0.0440(7)	0.012(1)
O5	1.0	0.5587(9)	–0.0701(6)	0.1955(3)	0.0145(9)
O6	1.0	0.0820(8)	0.0636(6)	0.2048(3)	0.0150(8)
O7	1.0	0.3889(8)	0.0549(6)	0.1975(4)	0.0164(7)
O8	1.0	–0.122(1)	–0.0569(7)	0.2008(6)	0.017(2)
K1	0.5	0.4487(9)	0.2408(8)	0.1347(4)	0.0188(7)
K2	0.5	0.428(1)	0.2654(6)	0.0708(5)	0.0206(8)
O9	1.0	0.285(2)	0.2691(8)	0.2625(8)	0.0191(9)
O**	1.0	0.088(2)	0.255(3)	0.402(1)	0.073(6)

* $U_{eq} = \dfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

** The oxygen of the water molecule. § with E.S.D. in parentheses.

The structural formula for zippeite deduced from the refinement is $K(UO_2)_2SO_4(OH)_3\cdot H_2O$. The density, measured in toluene using a pycnometer at room temperature, is 4.8 g cm^{-3} (mean of five determinations), in good agreement with the calculated value of 4.696 g cm^{-3}, which is based on the structure solution.

STRUCTURE DESCRIPTION

Zippeite possesses a layer structure. The U and S coordination polyhedra are located in layers parallel to (010) and are interconnected parallel to b through K$^+$, OH$^-$, and a water molecule (Fig. 4).

The coordination polyhedron around uranium is a pentagonal bipyramid similar to that found in other uranyl sulfate compounds (Niinistö *et al*. 1978, 1979, and references cited therein). Each U atom is surrounded by two apical uranyl oxygen atoms and by three equatorial hydroxyl groups and two equatorial oxygen atoms of sulfate. The $UO_4(OH)_3$ polyhedra form zigzag chains along the a axis by sharing equatorial OH-pairs (Fig. 4). In this way, a polymeric chain is built up from dimers of uranium atoms bonded by double OH-bridges. These linked double polyhedra are connected to other $UO_4(OH)_3$ chains on both sides by chains of S polyhedra to form the layers parallel to (010). Zippeite is the only compound reported to date that contains this pattern of linked double uranyl polyhedra. A comparable, also layered, but by far less dense arrangement of double polyhedra has been found in johannite (Mereiter 1982), another basic uranyl sulfate. The asymmetric unit of zippeite contains two U atoms, U1 and U2. The U2 atom, which is positioned at nearly the same y and z position as U1 but is shifted by *ca.* $a/2$ in x, is responsible for the observed pseudosymmetry. The U–U distances within the dimers are U1–U1 = 3.709(2), U2–U2 = 3.699(2), and U1–U2 = 3.699(2) Å. Both U atoms form distorted uranyl groups (O1 + O1') and (O2 + O2'), respectively, in which the average U–O bond length is 1.77(3) Å and the average angle O–U–O is 168(6)°. The distances between U and the equatorial O atoms range from 2.25(1) to 2.48(1) Å. Least-squares planes through the equatorial atoms demonstrate that these atoms deviate significantly from a coplanar arrangement. The distances of the oxygen atoms from these planes range from –0.37(1) to 0.38(1) Å for the oxygen atoms around U1 and from –0.11(1) to 0.08(1) Å for those around U2. The distances from the least-squares plane to U1 and U2 are –0.052(7) and –0.132(1) Å, respectively. The U–O3 and U–O4 distances [average, 2.32(4) Å] are comparable to the values found in other compounds with a double hydroxyl bridge (Åberg 1969, Viossat *et al*. 1983, Mereiter 1982, Perrin 1976, Legros & Jeannin 1975a, b). The distances from U to the sulfate oxygen atoms are longer [average: 2.47(1) Å].

The O3 and O4 oxygen atoms are bonded to three uranium atoms. The sum of the angles is 347.9(6)°
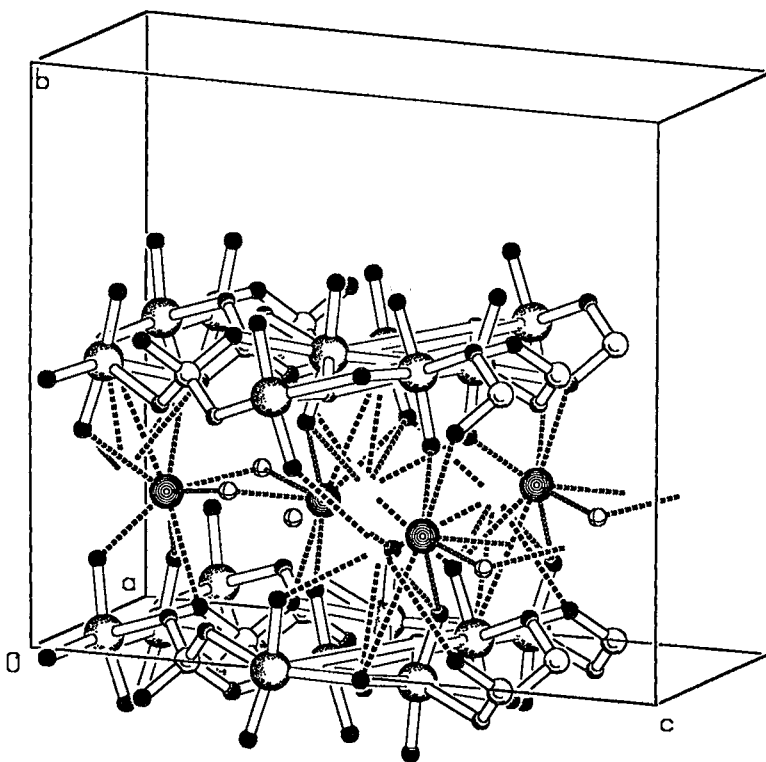
FIG. 3. Schematic representation of the crystal structure of synthetic zippeite.

around O(3) and 359.9(6)° around O4, not far from a trigonal planar configuration. In accord with the electroneutrality principle, these two oxygen atoms should be part of hydroxyl groups. Analysis of the bond distances shows that each hydroxyl oxygen (O3 and O4) is surrounded only on one side of the layer by three oxygen atoms at distances plausible for hydrogen bonds [2.57(2), 2.65(2), 2.93(2) Å to O3, and 2.76(2), 2.90(2), 2.93(2) Å to O4]. Bond-valence sums for O3 (1.86 vu) and O4 (2.21 vu), based on the coefficients of Brown & Altermatt (1985) and taking into account the appropriate valence units for H-bonds derived from the plot $versus$ O...H distance, are in good agreement with this statement. Bond-valence sums for U1 and U2 (6.9 and 6.7 vu) are rather high. Configurations most similar to these tricoordinated oxygen atoms occur in uranyl germanates (Legros & Jeannin 1975a, b).

The double polyhedra chains are joined by SO_4 bridging groups into an infinite $(UO_2)_2(OH)_2SO_4$ layer. The sulfate tetrahedra are distorted from a regular tetrahedron. The angles range from 102.7(4) to 118.9(4)° [average: 109(5)°], and the average S–O distance is 1.47(1) Å. Bond-valence sums are 6.02 vu for S1 and 6.10 vu for S2.

Two $(UO_2)_2(OH)_2SO_4$ sheets sandwich planar layers of K^+, OH^-, and H_2O polyhedra at b = ¼ and ¾. The linkage between the sheets is dominated by hydrogen bonds and coulombic interactions resulting in the micaceous cleavage of the mineral.

The K^+ cation is disordered over two positions, K1 and K2, each with a fractional (50%) occupancy. The K^+–K^+ distance is 1.15 Å. Bond-valence sums are 1.14 vu for K1 and 1.02 vu for K2. Each potassium ion is coordinated by an irregular polyhedron of eight oxygen atoms as shown in Figure 4, in which K2 is omitted for clarity. One of these oxygen atoms, O9, does not belong to a uranyl or sulfate group, but is situated in an interlayer position and bonds to the K^+, with a bond length of 2.62(1) Å. It occupies a site with no disorder, but some caution is necessary here because the final difference-Fourier map shows two small positive peaks (at approximately 2 eÅ⁻³) at short distances (1 Å) from O9. The O9 position could have been refined with a very high temperature-factor encompassing the surrounding small peaks, or the latter could have been refined as separate atoms, each with fractional occupancy. It is important to emphasize that there is some excess electron density in the vicinity
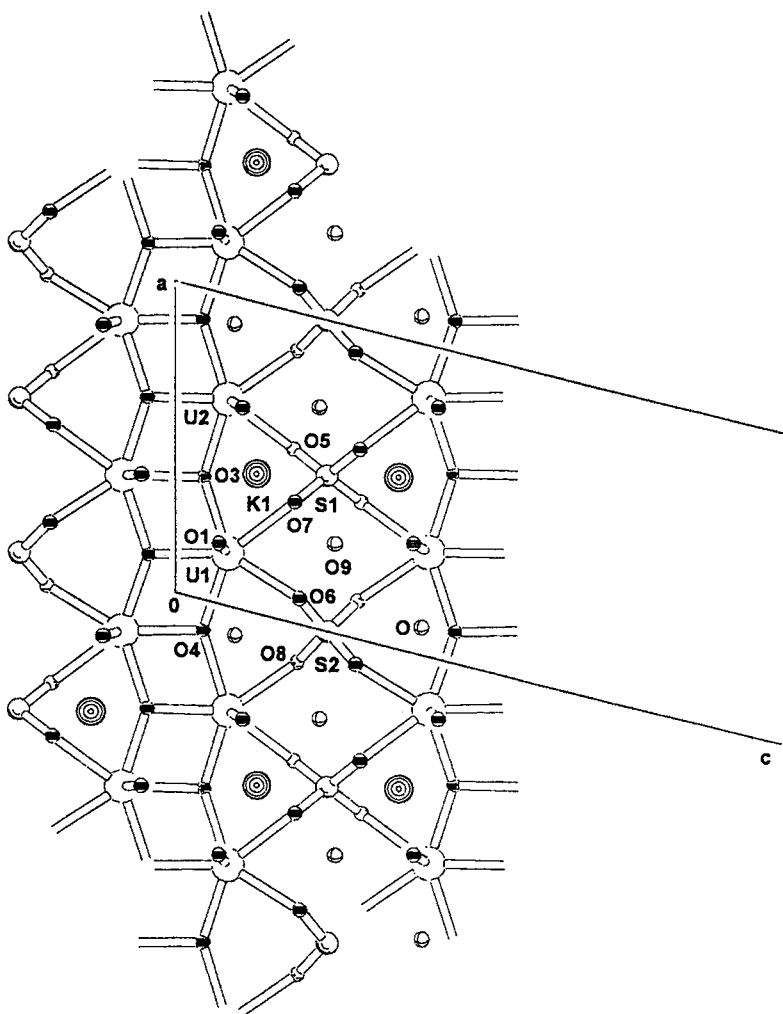
FIG. 4. Schematic representation of the crystal structure of synthetic zippeite: a cross-section through the $(UO_2)_2(OH)_2SO_4$ layer in the a–c plane.

of the O9 position, but refining these positions as separate atoms with low fractional occupancy-factors was judged to be meaningless in a map dominated by heavy atoms like uranium. The distances O9–K [2.616(14) and 2.689(17) Å] are close to the K–OH distance (2.689 Å) in potassium hydroxide (Jacobs *et al.* 1985). Combined with the fact that the bond-valence sum to O9 is 1.37 *vu*, this fact strongly suggests that O9 belongs to an OH group. In this way the local charge-balance also is ensured.

The oxygen (O) of the only water molecule in the structure is located at a fully occupied site with a high displacement-factors. As the hydrogen atoms could not be located, information about hydrogen bonds can

only obtained from an inspection of interatomic distances. Two of them, O–O1' [2.81(4) Å] and O–O2' [2.82(3) Å], are good candidates for hydrogen-bond distances. The other four distances [O–O1, 3.04(4); O–O2, 3.13(4); O–O3, 3.16(4); O–O5, 3.09(4) Å] can only represent weak bonding interactions at the most.

The composition derived from the crystallographic data is in good agreement with the one found by chemical analysis, with the exception of potassium. The higher content of potassium in the chemical analysis can be explained by the adsorption of small quantities of K$^+$ ions on the crystal surfaces, which is a well-known phenomenon.

The powder X-ray diffraction spectrum and indexing scheme were calculated from the refined atomic parameters by the program DISPOW of the NRCVAX package (Gabe *et al.* 1989). The results are given in Table 2.

LUMINESCENCE SPECTRA

Observations on the fluorescence of natural zippeite are not uniform. Some naturally occurring specimens fluoresce golden yellow, whereas other specimens fluoresce bright yellow to yellow-green or olive green, and some fluoresce only weakly. Frondel (1958) and Robbins (1983) reported that some samples of zippeite do not fluoresce at all and that the degree of hydration is responsible for the variation in the fluorescence.

The synthetic zippeite described here shows a moderate yellow-green fluorescence both under short- and long-wave ultraviolet radiation. The fluorescence spectra were recorded by means of a Perkin Elmer MPS 44B spectrofluorimeter at 298 and 77 K, using an excitation wavelength of 380 nm. Both spectra are represented with the same amplification in Figure 5.

The fluorescence at 298 K is characterized by a broad band between 520 and 620 nm, having a maximum at 551 nm. Unlike in the fluorescence spectra of other uranyl compounds (Vochten *et al.* 1993), no separate fluorescence bands could be detected in the 298 K spectrum. The intensity of the spectrum at 77 K is much higher than the one at 298 K,

a fact that can be explained by the decreasing quantum efficiency of fluorescence with increasing temperature. This effect reflects the improved probability for de-activation by external conversion due to increased frequency of collisions at elevated temperature. Moreover, a differentiation into three separate well-resolved bands at 535, 557 and 583 nm is observed at 77 K.

Based on the relation $E = hc/\lambda$, in which $hc = 1.9863\ 10^{23}$ Jm, E can be expressed in eV as $E = 1.24 \times 10^{-6} / \lambda$ (1 eV = 1.6021×10^{19} J). With this expression, the band gap energy E_g between the conduction and valence bands was calculated at the most intensive peak (535 nm) at 77 K as 2.3 eV. At this temperature, zippeite must be considered as a mineral with well-pronounced insulator properties.

INFRARED SPECTRUM

Čejka *et al.* (1985) studied the infrared spectra of zippeite extensively. According to these authors, the infrared spectra of different samples of zippeite are not uniform owing to the great variability of water bonding in the structure. The same authors also observed important differences in the band wavenumbers depending on the matrix in which the sample was recorded (KBr disc or nujol).

For this reason, we recorded the infrared spectrum of synthetic zippeite using an ATI Mattson Genesis FTIR spectrometer equipped with a Specac diffuse reflection unit. The spectrum is displayed in Figure 6.
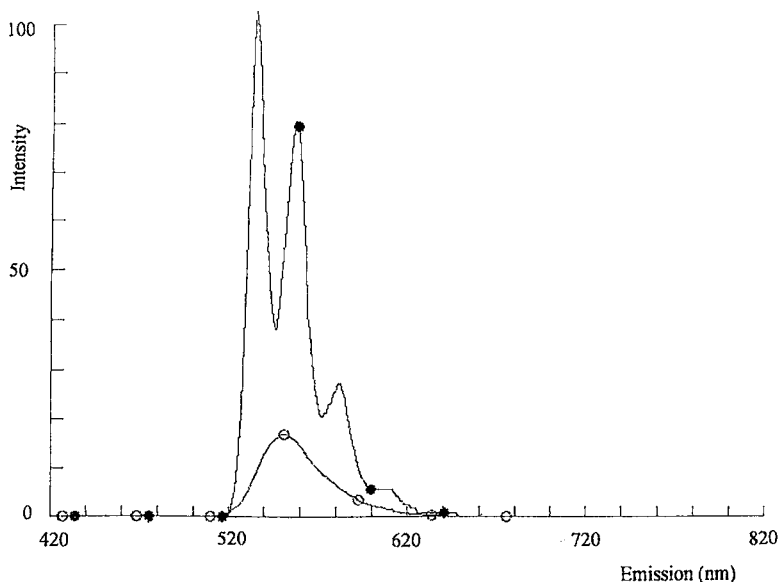

FIG. 5. Fluorescence spectra of synthetic zippeite at room temperature (○) and at 77 K (●).
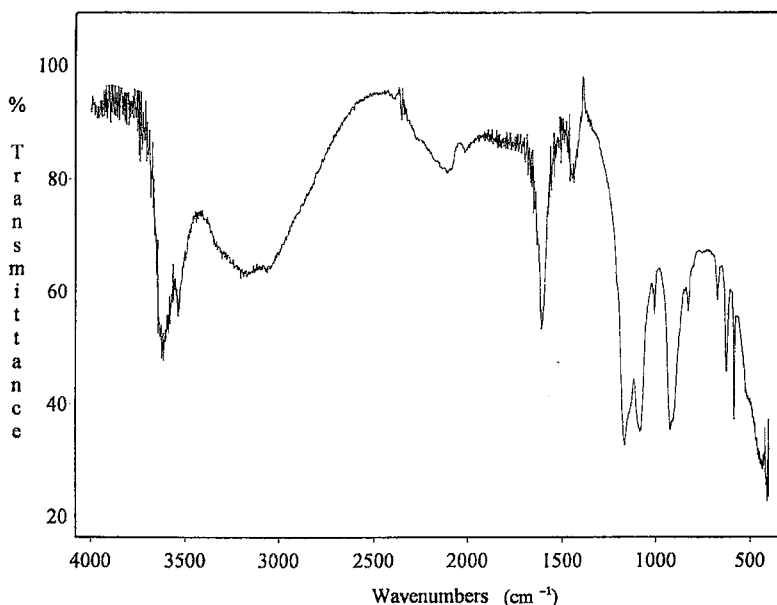
FIG. 6. Fourier-transform infrared spectrum of synthetic zippeite.

Table 5 lists the observed bands, together with those obtained by Čejka et al. (1985) and the assignments according to those authors. With the exception of some additional bands from the synthetic compound, the spectra agree very well. There are also some shifts in wavenumber that may be explained by the difference in the recording matrices used.

In the OH-stretching region, we observe two bands, at 3540 and 3625 cm^{-1}, whereas Čejka et al. (1985) observed only one band at 3504 cm^{-1}. According to Wilkins & Ito (1967), two OH-stretching vibrations may occur in layered silicates at 3625 and 3540 cm^{-1}. The bands at 1442 and 829 cm^{-1} may be attributed to different OH-deformation modes. A relatively strong and broad band is found at 3172 cm^{-1} and is assigned to a H_2O-stretching vibration. According to Farmer & Russell (1971), a broad band below 3200 cm^{-1} is observed when small, strongly polarizing cations are present in the structure. This effect is due to the fact that coordination of these small cations to water molecules in the structure causes the latter molecules to form stronger hydrogen bonds with other water molecules. As a consequence, the wavenumber of the H_2O-stretching vibration is lowered. The remaining bands can be explained as overtones or combination bands.

OPTICAL DATA

Because the crystals are too small for direct measurement of $2V$, the value of $2V_x$ is calculated as 59°. The crystals are biaxial negative with pleochroic colors: X colorless, Y pale yellow, Z yellow (Z is parallel to the elongation). The indices of refraction, determined by means of liquids with known index of refraction, are α 1.625 ± 0.001, β 1.710 ± 0.002, and γ 1.740 ± 0.002. The compatibility index CI = 1 − (K_P/K_C), calculated using the Gladstone–Dale constants of Mandarino (1981), the mean index of refraction, and the density, is 0.0016, which indicates that the data for synthetic zippeite belong to the category "superior".

TABLE 5. INFRARED ABSORPTION BANDS: ZIPPEITE

Assignment	Observed	Čejka et al.*		Observed	Čejka et al.*
v_2 SO$_4$	434 cm^{-1}	438 cm^{-1}	v_3 SO$_4$	1082 cm^{-1}	1068 cm^{-1}
v_4 SO$_4$	584	581		1165	1155
	624	620	δ OH	1442	
δ OH	673	669	δ H$_2$O	1608	1628
δ OH	829		v H$_2$O	3172	
v_3 UO$_2$	924	911 (929)	v OH	3540	3504
v_1 SO$_4$	1005	1005		3625	

* Čejka et al. (1985).

SOLUBILITY AND SOLUBILITY PRODUCT

When zippeite is dissolved in aqueous solution, it dissociates according to the following scheme:

$$K(UO_2)_2SO_4(OH)_3 \cdot H_2O \rightleftharpoons K^+ + 2UO_2^{2+}$$
$$+ SO_4^{2+} + 3OH^- + H_2O$$
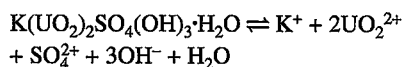
With this dissociation, a solubility product K_{sp} can be defined as

$$K_{sp} = [K^+] \cdot [UO_2^{2+}]^2 \cdot [SO_4^{2-}] \cdot [OH]^3$$

The solubility was measured by adding distilled water to a sufficient amount of zippeite, after which the solution was stirred for at least 1 week to give the solid – solution system the opportunity to equilibrate. During this period, the temperature was kept at 25°C. After equilibration, the solution was filtered off, and the total uranyl content was determined. The measurements were then repeated using different K_2SO_4 solutions instead of distilled water. This yielded information on how the solubility varies with both increasing $[K^+]$ and $[SO_4^{2-}]$ and with the ionic strength. The results of these measurements are gathered in Table 6. This table shows first of all a decrease of the solubility with increasing K_2SO_4 concentration. This fact confirms that both $[K^+]$ and $[SO_4^{2-}]$ play an important role in the solubility product as it is presented above.

The dissociation scheme suggests that, when zippeite goes into solution, a significant increase in the pH of the solution is to be expected because a relatively large amount of OH^- ions is set free. This effect should be more important if the solubility increases. Table 6 shows, however, that the pH for all solutions used in our experiments has a relatively acidic value, ranging from 4.5 to 4.7. This may be explained by the formation of uranyl-hydroxo complexes, which is traditionally represented as

$$p\ UO_2^{2+} + p\ H_2O \rightleftharpoons [UO_2]_p[OH]_q^{2p-q} + q\ H^+$$
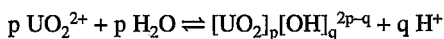
With these reactions we can associate the formation constants β_{pq} defined as

$$\beta_{pq} = \frac{[(UO_2)_p(OH)_q^{2p-q}] \cdot [H^+]^q}{[UO_2^{2+}]^p}$$

Djogic *et al.* (1986) discussed the most significant uranyl-hydroxo complexes and list their formation constants, β_{pq}. Owing to the presence of these complexes, the concentration of the free uranyl ions will be lowered considerably. The total uranyl concentration, being the concentration of all uranyl-bearing species together, may be expressed as:

$$C_{UO2} = [UO_2^{2+}] + \sum_{p,q} p \cdot [(UO_2)_p(OH)_q^{2p-q}]$$

$$= [UO_2^{2+}] + \sum_{p,q} p \cdot \frac{\beta_{pq}[UO_2^{2+}]^p}{[H^+]^q}$$

In this expression, the summation stands for all known uranyl hydroxo complexes. If this equation is solved, the actual $[UO_2^{2+}]$ can be obtained. Complexes between UO_2^{2+} and SO_4^{2-} also exist (Djogic *et al.* 1986), but the $[UO_2^{2+}]$ resulting from the above calculations is very low, and the formation constants of the uranyl sulfate complexes are not large enough to represent any significant formation of the latter species.

Using the above considerations, the solubility product of zippeite is determined for each of the given ionic strengths. These values also are given in Table 6. Extrapolation to zero ionic strength yields a solubility of $6.93.10^{-2}$ M and a pK_{sp} value of 42.60. This value for pK_{sp} is very large, and the corresponding K_{sp} is therefore very low. The latter result is not surprising. The presence of the OH^- ions in the expression for the solubility product accounts on its own for a pK_{sp} of 27.9 – 28.5. Given the fact that the UO_2^{2+} ions are present at a very low concentration, owing to the formation of the above-cited complexes, it is to be expected that pK_{sp} is very high. Therefore, a moderate solubility is here associated with a very low solubility product.

TABLE 6. SOLUBILITY DATA: ZIPPEITE

Medium	pH	Ionic strength	Solubility*	pKsp
H₂O	4.51	0.0044	653.4	41.37
0.003 M K₂SO₄	4.45	0.0127	546.0	39.81
0.007 M K₂SO₄	4.51	0.0239	430.5	39.19
0.020 M K₂SO₄	4.71	0.0609	134.4	38.67
0.040 M K₂SO₄	4.61	0.1208	114.0	38.33
Extrapolation		0	693.0	42.60

* Units: 10^{-6} mol/L.

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