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SPECTROSCOPIC CHARACTERIZATION OF SYNTHETIC BECQUERELITE, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$, AND SWARTZITE, $\text{CaMg}[\text{UO}_2(\text{CO}_3)_3] \cdot 12\text{H}_2\text{O}$

SAMER AMAYRI[§], THURO ARNOLD, HARALD FOERSTENDORF,
GERHARD GEIPEL AND GERT BERNHARD

Forschungszentrum Rossendorf, Institut für Radiochemie, P.O. Box 510119, D-01314 Dresden, Germany

ABSTRACT

Becquerelite, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$, and swartzite, $\text{CaMg}[\text{UO}_2(\text{CO}_3)_3] \cdot 12\text{H}_2\text{O}$, have been synthesized and identified by X-ray powder diffraction (XRD). Chemical compositions were verified by ICP-MS and AAS. Time-resolved laser-induced fluorescence spectroscopy (TRLFS) and Fourier-transformed infrared spectroscopy (FTIR) were used for the first time to characterize these phases. In becquerelite, there are four fluorescence emission bands, at 518.9, 535.6, 553.4, and 578.9 nm, and a characteristic fluorescence lifetime of $3.1 \pm 0.2 \mu\text{s}$. Swartzite shows six characteristic fluorescence emission bands, at 472.3, 488.9, 509.0, 531.1, 554.7, and 578.9 nm, and a fluorescence lifetime of $59.4 \pm 0.1 \mu\text{s}$. The FTIR spectra of becquerelite are characterized by an intense asymmetric stretching vibration ($\nu_3 \text{UO}_2^{2+}$ mode) band at 946 cm^{-1} , with shoulders at approximately 925 and 902 cm^{-1} . Swartzite shows its characteristic $\nu_3 \text{UO}_2^{2+}$ mode of the uranyl cation at 898 cm^{-1} . As natural U^{6+} -bearing samples commonly form thin coatings on rock or mineral surfaces or as a component mixed with other solids, it is generally difficult to identify small quantities of these secondary phases. Spectroscopic methods like TRLFS and FTIR spectroscopy are found to be promising methods to identify such secondary phases.

Keywords: uranium, synthesis, TRLFS spectroscopy, FTIR, spectroscopy.

SOMMAIRE

Nous avons synthétisé la becquerelite, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$, et la swartzite, $\text{CaMg}[\text{UO}_2(\text{CO}_3)_3] \cdot 12\text{H}_2\text{O}$, et nous les avons identifiées par diffraction X, méthode des poudres. Leur composition chimique a été vérifiée par analyses ICP-MS et AAS. Nous nous servons ici pour la première fois de la résolution temporelle de la spectroscopie de la fluorescence induite par laser (TRLFS) et la spectroscopie dans l'infrarouge avec transformation de Fourier (FTIR) pour caractériser ces phases. Dans la becquerelite, il y a quatre bandes d'émission de fluorescence, à 518.9, 535.6, 553.4, et 578.9 nm, et une durée de fluorescence caractéristique de $3.1 \pm 0.2 \mu\text{s}$. La swartzite fait preuve de six bandes d'émission de fluorescence caractéristiques, à 472.3, 488.9, 509.0, 531.1, 554.7, et 578.9 nm, et une durée de fluorescence de $59.4 \pm 0.1 \mu\text{s}$. Les spectres FTIR de la becquerelite montrent une bande de vibration d'étirement asymétrique intense caractéristique (mode UO_2^{2+} , ν_3) à 946 cm^{-1} , avec satellites près de 925 et 902 cm^{-1} . Dans la swartzite, la bande caractéristique du mode UO_2^{2+} ν_3 du cation uranyle se trouve à 898 cm^{-1} . Les échantillons naturels de phases secondaires contenant U^{6+} se présentent généralement sous forme de minces pellicules à la surface de roches

[§] Present address: Institut für Kernchemie der Universität Mainz, Fritz-Strassmann Weg 2, D-55128 Mainz, Germany. E-mail address: amayri@uni-mainz.de

ou de minéraux, ou bien comme composants de mélanges avec d'autres solides. Il est donc difficile, en général, d'identifier ces matériaux en petites quantités. Les méthodes spectroscopiques telles TRLFS et FTIR semblent prometteuses pour fins d'identification de telles phases secondaires.

(Traduit par la Rédaction)

Mots-clés: uranium, synthèse, spectroscopie TRLFS, spectroscopie FTIR.

INTRODUCTION

Minerals containing hexavalent uranium are commonly found in small quantities in the vicinity of uranium orebodies, uranium mill tailings and other environments related to uranium mining activities. The solubility of secondary U^{6+} phases, together with adsorption reactions, are likely to play an important role in controlling the source term for the uranium migration (Murphy 1997, Sandino & Grambow 1994) through geological materials, *e.g.*, solid rocks, unconsolidated tailing material and soils. Hence, the mineralogical identification of even minor amounts of secondary uranium phases is a necessity to develop a better understanding of the chemistry of uranium in contaminated environments. Such an understanding may eventually lead to effective remediation techniques for contaminated ecosystems and also may improve performance assessments with respect to human and ecological health risks. Here, we focus on the spectroscopic characterization of synthetic becquerelite and swartzite as an illustration of our approach.

BACKGROUND INFORMATION

Phases containing hexavalent uranium near contaminated sites are generally identified with classical methods, *e.g.*, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy with energy-dispersion spectroscopy (SEM-EDS), and acid digestion with subsequent chemical analysis. However, many of these secondary uranium phases occur as a coating on rock surfaces or in mixtures with other minerals, so that their isolation from the surrounding matrix is tedious, time-consuming and possibly misleading. With classical methods only, one is not always able to undoubtedly identify thin coatings of secondary phases of uranium and their chemical composition. New refined spectroscopic techniques provide alternatives to the classical methods. Fourier-Transformed InfraRed spectroscopy (FTIR) requires only micrograms of sample material, and the non-destructive Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS), only a few μm^2 of sample area. The fluorescence spectrum of the mineral can then be used as a fingerprint to determine the mineralogy of coatings on rock surfaces. Furthermore, such fluorescence data can be used in an interpretation of spectra of unknown uraniferous samples (Geipel *et al.* 2000).

In this study, two synthetically prepared phases containing U^{6+} becquerelite, $Ca[(UO_2)_6O_4(OH)_6] \cdot 8H_2O$, and swartzite, $CaMg[UO_2(CO_3)_3] \cdot 12H_2O$, were investigated with FTIR spectroscopy and TRLFS. During the oxidative dissolution of UO_2 , uranyl hydroxides, commonly schoepite, are formed (Bruno *et al.* 1995). However, the formation of the schoepite is a transient event, and it is not considered the long-term stable phase (Bruno *et al.* 1995, Wronkiewicz *et al.* 1992). In the presence of alkali and alkaline-earth elements and depending on external parameters like pH and ground-water composition, schoepite undergoes further transformation (Finch & Murakami 1999) into a sequence of secondary U^{6+} phases and uranyl oxyhydroxides, among others becquerelite (Sowder *et al.* 1996, Vochten & Van Haverbeke 1990, Burns *et al.* 1997). Becquerelite has also been identified as a product in the oxidative corrosion of synthetic $UO_2(s)$ (Wronkiewicz *et al.* 1992, 1996). It is yellow, in some cases orange, and mostly massive. Tabular crystals of 3 cm have been observed at the Shinkolobwe mine (Pagoaga *et al.* 1987).

Swartzite is found in association with bayleyite, andersonite and schrockingerite. It has only a narrow field of stability in the system $Ca^{2+} - Mg^{2+} - [UO_2(CO_3)_3]^{4-} - H_2O$ (Mereiter 1986). Swartzite has been established as one of the end products in alkaline carbonate environments, such as at the Hillside mine, near Bagdad, Arizona. Swartzite also was found in localities of the Colorado Plateau, such as the Coral Claim in Utah (Axelrod *et al.* 1951). Swartzite is a yellowish green mineral, which becomes very pale yellow upon dehydration. It shows bright yellowish green fluorescence.

MATERIALS AND METHODS

The synthesis of becquerelite and swartzite

Becquerelite, $Ca[(UO_2)_6O_4(OH)_6] \cdot 8H_2O$, was synthesized by stoichiometric mixing of uranyl nitrate solution (19.49 g $UO_2(NO_3)_2 \cdot 6H_2O$, p.a., Merck in 100 mL) and calcium nitrate solution (1.489 g $Ca(NO_3)_2 \cdot 4H_2O$, p.a., Merck in 10 mL) at room temperature under constant stirring. An initial pH of 2.16 was measured for this mixture. The pH was then adjusted to 3.60 by addition of sodium hydroxide solution. After two weeks, the precipitation of a yellow powder was observed. The powder was filtered, washed several times with MilliQ-water to remove any excess reactants, and dried at room temperature.

Swartzite, $\text{CaMg}[\text{UO}_2(\text{CO}_3)_3] \cdot 12\text{H}_2\text{O}$, was prepared using instructions given by Meyrowitz (1962). Swartzite was synthesized under constant stirring by slowly adding 13.5 mL of an aqueous solution containing 2.7 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.85 mol) to 60 mL of an aqueous solution containing 12.4 g of synthetic bayleyite $\text{Mg}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 18\text{H}_2\text{O}$ (0.25 mol/L). Bayleyite was prepared according to a procedure described by Amayri (2002). The prepared solution was allowed to stand for 24 hours. Subsequently, the solution was filtered, and the filtrate was allowed to evaporate at room temperature. After approximately three weeks, needle-like prisms of swartzite of up to several millimeters in length were observed. The prisms obtained were quickly washed three times with MilliQ-water and subsequently air-dried.

Nitric acid digestion and chemical analysis

The air-dried synthetic compounds were dissolved in 10% HNO_3 (Suprapur, Merck). The uranium content was determined using an inductively coupled plasma (Ar plasma) – mass spectrometer (ICP–MS) (Elan 500, Perkin Elmer, Überlingen, Germany). The concentration of the alkaline-earth metals Mg, Ca was determined by flame-atomic absorption spectrometer (AAS 4100, Perkin Elmer, Überlingen, Germany). The results of the chemical analysis of the synthesized becquerelite and swartzite obtained by ICP–MS and AAS correspond very well within analytical errors to their respective theoretical values. The analytical results clearly indicate that the synthesis of becquerelite and swartzite as pure phases was successful.

X-ray powder diffraction

The X-ray powder-diffraction analysis of the two uranium solids were recorded with a Universal-Röntgen-Diffraktometer (URD 6, Freiburger Präzisionsmechanik, Freiberg, Germany) using $\text{CuK}\alpha$ ($\lambda = 0.1542 \text{ nm}$) at 40 kV and 30 mA. Silicon powder was used as an external standard. The diffractometer was operated in Bragg–Brentano geometry in a step mode with a step width of 0.05° . The X-ray-diffraction spectra were recorded in the 2θ range from 5° to 60° . The Diffracplus Evaluation program, Version 2.2 (Siemens AG, Germany) was used for data processing, for reflection indexing and refining. The d values, the normalized intensities (I/I_0) and the cell parameters (a , b , c) were calculated after peak fitting from an acquired spectrum with the external silicon standard with the program Win-Metric Version 3.04 (SIGMAC GmbH, Germany).

The cell parameters of our samples are in accordance with accepted values for becquerelite (Pagoaga *et al.* 1987) and swartzite (Mereiter 1986). The reflections obtained were identified by matching them with known powder diffractograms of becquerelite and swartzite

(PDF 29–389 and 85–970). The samples were stored in an ambient atmosphere at a humidity of 60% for six months. X-ray-diffraction patterns were recorded subsequent to the synthesis of the mineral and after a six-month period of storage. No differences were recorded, indicating that the synthesized minerals are stable in air.

Scanning electron microscopy with energy-dispersion spectrometry

The crystals of swartzite were crushed in a mortar prior to SEM sample preparation. Both specimens were then fixed on separate SEM sample holders and either gold-coated for microscopic characterization in secondary electron (SE) detection mode or sputtered with carbon for energy-dispersion spectrometry (EDS) analysis. The samples were investigated by scanning electron microscopy (SEM, Mod. Zeiss DSM 962). The applied acceleration voltage was in the range 15 to 30 keV.

The appearance of becquerelite is consistent with observations made by Pagoaga *et al.* (1987) and Wronkiewicz *et al.* (1992): solitary yellow rectangular plates are flattened on [001] and striated parallel to [001]. Wronkiewicz *et al.* (1992) also described becquerelite as dark yellow tabular crystals. Results of EDS analyses of becquerelite confirm the results of the chemical analyses described above. The EDS spectrum of becquerelite shows the $\text{CaK}\alpha$ line on the right shoulder of the $\text{UM}\beta$ peak at approximately 3.5 keV. Similar observations were made by Wronkiewicz *et al.* (1992).

The morphology of swartzite is in accordance with the description given by Mereiter (1986): the lath-like prisms are elongate along [001]. The EDS spectrum confirms the chemical composition and purity of the synthesized swartzite.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

Laser pulses from a Nd-YAG laser (SL 401–20, Spectron Laser Systems) were applied to the solid samples of becquerelite and swartzite. The actual laser power was monitored with an optical energy meter (model 1835, Newport, Corp., Irvine, California, to allow for corrections due to the oscillation in laser energy. The fluorescence signal was focused into a fiber optic cable that was coupled to the slit of a triple grating spectrograph (M 1235, EG&G). The fluorescence spectra are measured by a gate diode array (M 1475, EG&G). The spectra were collected with a controller (M 1471A, EG&G). A more detailed description of the experimental set-up can be found in Geipel *et al.* (1996). An excitation wavelength of 266 nm was used. The spectra were recorded in the range from 450 to 600 nm, with delay times ranging from 0.1 μs to 100 μs after the application of the laser pulse. The gate time was 1 μs . The actual laser energy was 400 μJ . For every delay time, the fluorescence signal was averaged by sampling three single spectra over 100 laser

shots. All functions (time controlling, device settings, correction of energy, reading the spectra, data storage) of the spectrometer are computer-controlled. The computer software Grams/386TM (Galactic Industries Corp., Woburn, Massachusetts) was used for deconvolution of the spectra. The time dependencies of the spectra were calculated with the Origin 6.1G Client (Microcal Software Inc., Northampton, Massachusetts) and Excel 2000® programs. The samples were measured at ambient temperature and at a relative humidity of 60 $\pm$ 2%.

Fourier-transformed infrared spectroscopy (FTIR)

The FTIR spectra were recorded using a Perkin Elmer GX-2000 instrument equipped with an Mercury Cadmium Telluride (MCT) detector. Spectral resolution of all spectra was 4 cm^{-1} in the frequency range from 4000 to 600 cm^{-1} . For acquisition of the absorption spectra, the compounds were prepared as KBr pellets. Diffuse-reflectance infrared Fourier transform (DRIFT) measurements were accomplished by mixing the crystalline compounds with solid KBr. The concentration of the samples was approximately 0.2 wt%.

RESULTS AND DISCUSSION

Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

Detailed spectral information of uranium minerals is incomplete (Robbins 1983, Geipel *et al.* 2000). How-

ever, recently TRLFS investigations of some uranium phosphates and uranium arsenates (Geipel *et al.* 2000), as well as several uranium carbonates (Amayri 2002), have been described.

Generally, solid U^{6+} minerals are characterized on the basis of wavelength of the emission bands and the characteristic lifetime of the fluorescence. Such an absorption spectrum then can be used to characterize, or to "fingerprint", fluorescent uranium minerals (Geipel *et al.* 2000). The fluorescence data obtained may also provide a link to solution spectra of known and so far unknown aqueous species of U^{6+} in contaminated environmental waters (Amayri 2002).

The fluorescence spectrum of becquerelite is shown in Figure 1. The full-width-half-maximum (FWHM) of the individual peaks in the measured fluorescence spectrum of becquerelite is in the range of 16 to 20 nm. In respect to deconvolute the spectrum to extract the characteristic emission peaks, this is a rather poor FWHM value. For comparison, the FWHM value for the free uranyl ion UO_2^{2+} , equal to 10 to 12 nm, makes the peak deconvolution process easier and more precise. The deconvoluted fluorescence spectrum of becquerelite reveals four characteristic intense fluorescence emission bands at 518.9, 535.6, 553.4, and 578.9 nm. The respective characteristic fluorescence lifetime of 3.1 $\pm$ 0.2 μs of becquerelite is calculated here for the first time from the TRLFS spectrum shown in Figure 2.

Swartzite shows a characteristic fluorescence spectrum comprising a set of evenly spaced absorption peaks (Fig. 3). The deconvoluted fluorescence spectrum re-

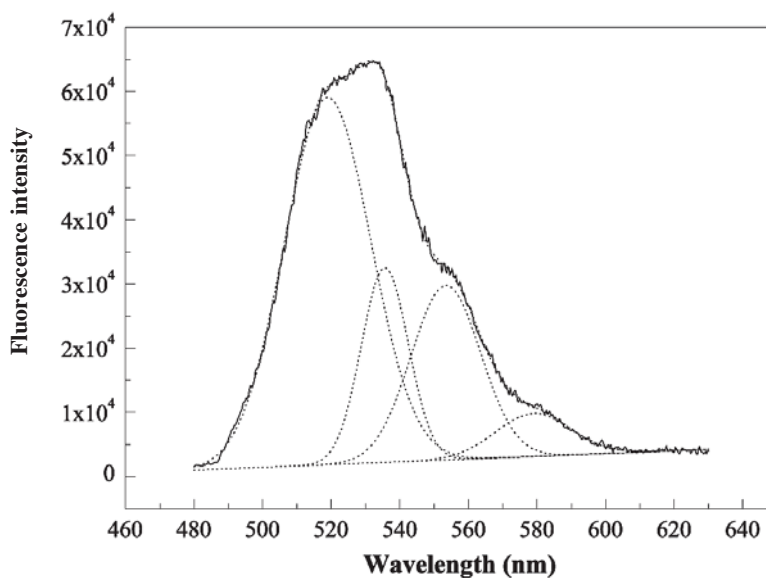


FIG. 1. Fluorescence spectra of synthetic becquerelite; dotted lines show the curve fit of the spectra (Gaussian shape).

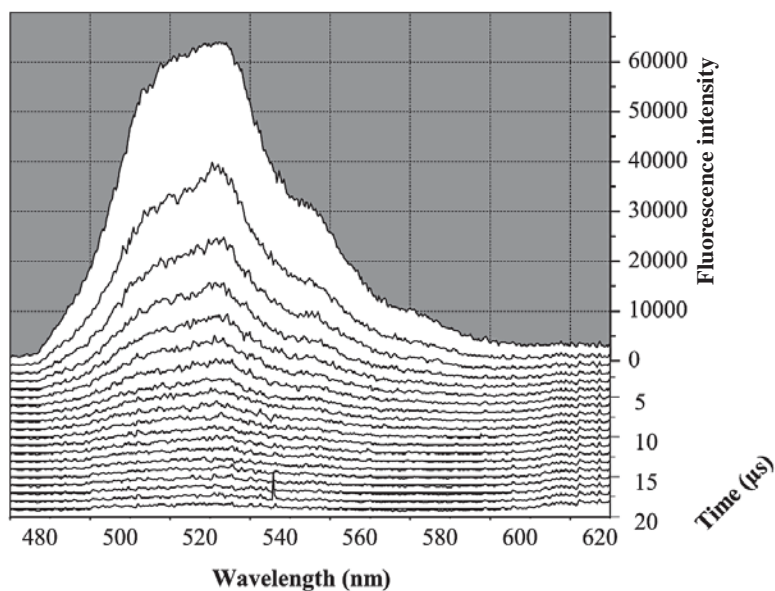


FIG. 2. Fluorescence spectra of synthetic becquerelite as a function of delay time.

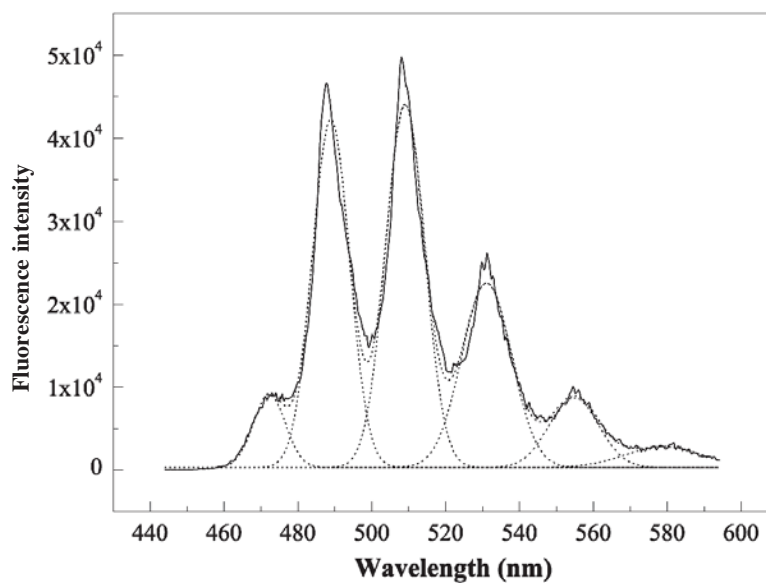


FIG. 3. Fluorescence spectra of synthetic swartzite; dotted lines show the curve fit of the spectra (Gaussian shape).

veal six characteristic intensive fluorescence emission bands at 472.3, 488.9, 509.0, 531.1, 554.7, and 578.9 nm. The characteristic fluorescence lifetime of $59.4 \pm 0.1 \mu\text{s}$ for swartzite is also calculated here for the first

time from the TRLFS spectrum (Fig. 4). The main fluorescence emissions of becquerelite and swartzite are listed in Table 1 in comparison with uranyl ions.

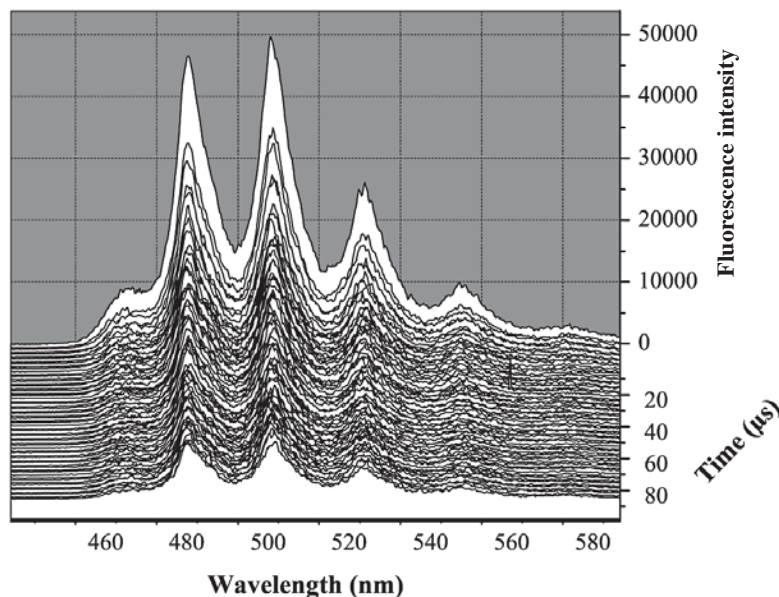


FIG. 4. Fluorescence spectra of synthetic swartzite as a function of delay time.

TABLE 1. FLUORESCENCE PROPERTIES OF SYNTHETIC BECQUERELITE AND SWARTZITE

Substance	fluorescence emission bands						lifetime
becquerelite $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$	-	-	518.9	535.6	553.4	578.9	3.1 ± 0.2
swartzite $\text{CaMg}[\text{UO}_2(\text{CO}_3)_3] \cdot 12\text{H}_2\text{O}$	472.3	488.9	509.2	531.0	554.7	578.9	59.4 ± 0.1
free uranyl ion $\text{UO}_2^{2+}(\text{aq.})$ pH 1.0; $I = 0.1 \text{ M}$	471.3	488.9	510.5	533.9	559.4	585.5	1.80 ± 0.8
uranyl tricarbonate ion $\text{UO}_2(\text{CO}_3)_3^{4-}$	no uranium fluorescence detectable at 25°C						

emission bands in nm, lifetimes in μs .

TABLE 2. COMPARISON OF THE RELEVANT BANDS IN THE FTIR SPECTRA OF BECQUERELITE

Becquerelite KBr pellet*	Becquerelite Čejka <i>et al.</i> (1998)	Tentative assignment
3436	3504	$\nu \text{ OH}$
1626	1625	$\delta \text{ H}_2\text{O}$
1415	1435	
1384	-	$\nu_3 \text{ NO}_3^-$
1300	-	
1275	1250	$\delta \text{ UOH in-plane}$
1004	997	$\delta \text{ UOH in-plane}$
946		
~ 920 sh		
~ 902 sh	927	$\nu_3 (\text{UO}_2^{2+})$
834	840	$\delta \text{ UOH in-plane (?)}$
816-818*	812	$\nu_1 \text{ UO}_2^{2+}$

sh: shoulder. * DRIFT (this work). Tentative assignments were adopted from Čejka *et al.* (1998). Band frequency in wavenumbers (cm^{-1}).

It is well known that the free uranyl ions show good fluorescence spectra with six characteristic fluorescence emission bands and a characteristic lifetime of $1.57 \pm 0.06 \mu\text{s}$ (Brachmann 1997). It is also well known that the uranyl tricarbonate ion, $\text{UO}_2(\text{CO}_3)_3^{4-}$, shows no fluorescence at all at 25°C (Bernhard *et al.* 2001). However, where alkaline earths such as Ca or Mg are a constituent of the solid or aqueous U^{6+} species, an intense fluorescence signal is obtained (Amayri 2002).

Infrared spectroscopy (IR)

Infrared spectroscopy is widely used in analyzing the composition of natural and synthetic samples. This non-destructive method provides characteristic spectra that

serve as fingerprints for the identification of minerals. This approach is very helpful in mineralogy, in particular where a specimen is very rare. The spectra of the synthetic minerals were recorded in transmission (KBr pellet) and with the diffuse reflectance (DRIFT) technique, since a different sample-preparation technique may have an effect on the shape of distinct spectral features.



The spectra of becquerelite are in excellent agreement irrespective of the acquisition technique (Fig. 5).

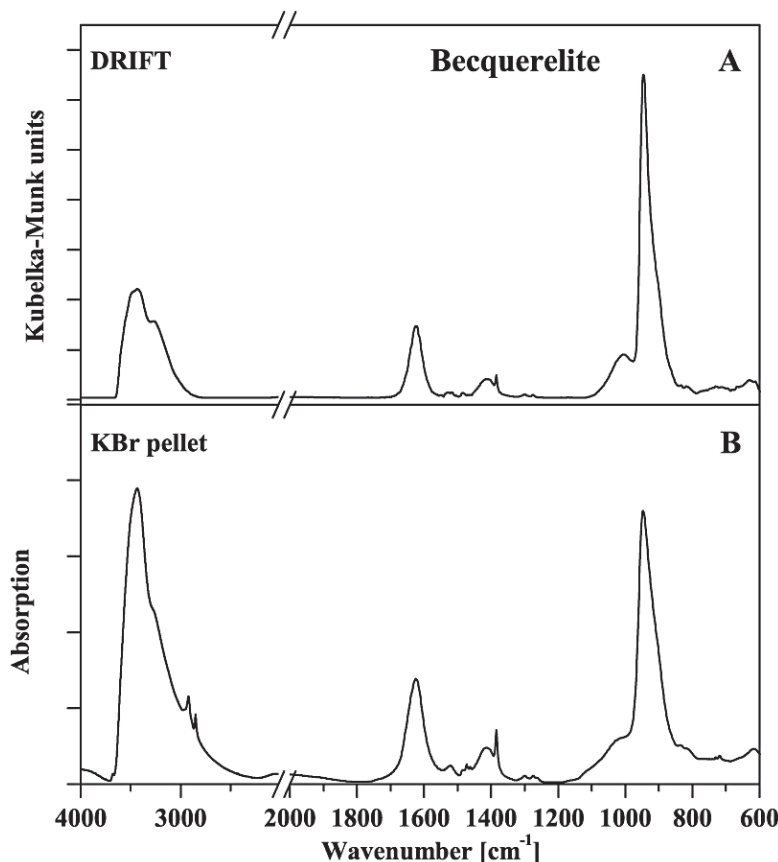


FIG. 5. FTIR spectrum of synthetic becquerelite.

Both spectra only show significant bands at 3436 and 1626 cm^{-1} , with slightly different relative intensities, which are assigned to ν OH-stretching and δ H_2O -bending vibrations, respectively. The sharp band at 1384 cm^{-1} was assigned to traces of nitrate as a result of the synthesis procedure. The presence of significant impurities (*e.g.*, formation of uranyl nitrate) in the synthetic phase is excluded, since the results of the XRD experiments as well as the SEM-EDS investigations clearly show that nitrate occurs at a trace level only.

The spectra of becquerelite are characterized by an intense band at 946 cm^{-1} showing shoulders at approximately 925 and 902 cm^{-1} . These findings are in accordance with spectra published by Čejka *et al.* (1998). However, the frequency of this band in our spectra is shifted approximately 20 cm^{-1} to higher frequencies (Table 2). We assume that this shift is either due to the different procedure of synthesis or to a different content of H_2O in the synthetic mineral, which leads to a strong superposition of UOH-bonding vibrations in this frequency range. A definitive explanation of this different observation cannot be given yet.

From the crystal structure of becquerelite, six structurally different uranyl cations (U1–6) were identified (Pagoaga *et al.* 1987). With respect to the interatomic distances between the uranium and the calcium atoms, three types of uranyl cations can be derived: three uranyl cations are directly linked to calcium *via* an oxygen showing relatively short U–Ca distances up to 4.2 Å (U1, U3, U6). A medium distance, about 4.6 Å, was found for U2. The longest U–Ca distance is approximately 5.6 Å for U4 and U5, respectively. From this variation of the distances, an influence of the frequency of the ν_3 UO_2^{2+} mode due to different hydrogen bonding and electrostatic interaction of the molecular environment can be expected. This structural heterogeneity may be reflected in the infrared spectra by the intense band at 945 cm^{-1} showing shoulders at 925 and 902 cm^{-1} .



The overall shapes of the FTIR spectra of swartzite (Fig. 6) correspond in large part to spectra of liebigit

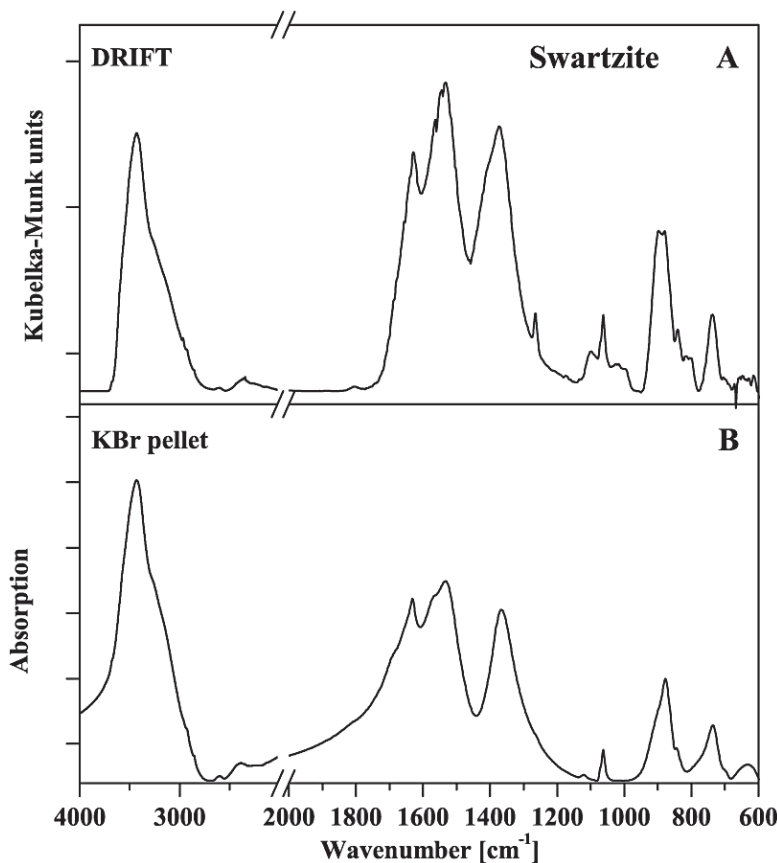


FIG. 6. FTIR spectrum of synthetic swartzite.

TABLE 3. COMPARISON OF THE RELEVANT BANDS IN THE INFRARED SPECTRA OF SWARTZITE AND LIEBIGITE

Swartzite KBr pellet*	Swartzite DRIFT*	Liebigite Urbanec & Čejka (1979)	Tentative assignment
3431	3431	3402	ν OH
1632	1629	1620	δ H ₂ O
1563 sh	1563 sh		
1534	1533	1537	ν_3 (CO ₃ ²⁻)
1367	1373	1385	split (bidentate)
1070 sh	1070 sh	1069	ν_1 (CO ₃ ²⁻) split
1063	1063		
898 sh	898	890	ν_3 (UO ₂ ²⁺)
877	880		ν_1 (UO ₂ ²⁺) or ν_2 (CO ₃ ²⁻) (?)
846	841	841	ν_2 (CO ₃ ²⁻)
737	737	737	
702 sh		682	ν_4 (CO ₃ ²⁻) split

sh: shoulder. Tentative assignments were adopted from Urbanec & Čejka (1979) and Čejka (1999). Band frequency in wavenumbers (cm⁻¹). * This work.

and bayleyite published elsewhere (Čejka 1999, Urbanec *et al.* 1979). The FTIR spectra reflect the great resemblance of their crystal structures. The spectra of swartzite shows a broad absorption band around 3431 and 1632 cm⁻¹, representing the ν OH-stretching and δ H₂O-bending vibration, respectively. The bands at 1533 and 1367 cm⁻¹ can be assigned to the split ν_3 mode of the CO₃²⁻ anions. This mode usually shows such a great split where the anion coordinates to a metal as a bidentate ligand (Nakamoto 2002). A splitting of the other CO₃²⁻ modes can also be expected owing to structural heterogeneity of the anions in the crystal. In fact, the crystal structure of swartzite shows two structurally different types of the CO₃²⁻ anions (Mereiter 1986). Two carbonates serve as a bridge between the uranyl and the calcium cations, whereas the third carbonate is merely bound to the uranium and to the H-bonding network of the H₂O molecules. Therefore, the shoulders of the bands at 1533, 1063 and 737 cm⁻¹ obviously represent this structural heterogeneity (Table 3).

The asymmetric stretching vibration of the uranyl cation ($\nu_3 \text{UO}_2^{2+}$) of uranyl tricarbonates is observed in the range between 925 and 840 cm^{-1} . In this region, the DRIFT spectrum of freshly prepared swartzite shows two overlapping bands with maximum at 880 and 898 cm^{-1} , respectively, whereas the absorption spectrum (KBr pellet) shows only one band at 877 cm^{-1} with a shoulder around 900 cm^{-1} . We assign the band at 898 cm^{-1} to the ν_3 mode of the uranyl cation, whereas the band at 880 cm^{-1} cannot unequivocally be assigned to a distinct mode. In this region, contributions of $\nu_1 \text{UO}_2^{2+}$, $\nu_2 \text{CO}_3^{2-}$ or other OH-modes have to be taken into account. A strong association to the OH-bonding network in the crystal can be suggested from the observation that upon storage of the synthetic phase at low humidity, the relative intensity of the band at 880 cm^{-1} decreases. Earlier FTIR investigators of uranyl tricarbonates found that an increasing frequency of the $\nu_3 \text{UO}_2^{2+}$ mode was observed with increasing content of H_2O and M^{2+} cations (Čejka 1999). For example, in liebigit, $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 10\text{H}_2\text{O}$, the ν_3 stretch of UO_2^{2+} was observed between 893 and 882 cm^{-1} , and in bayleyite, $\text{Mg}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 18\text{H}_2\text{O}$, it is found at 903 cm^{-1} (Amayri 2002). Consequently, the frequency of the $\nu_3 \text{UO}_2^{2+}$ mode in swartzite, $\text{CaMg}[\text{UO}_2(\text{CO}_3)_3] \cdot 12\text{H}_2\text{O}$, at 898 cm^{-1} confirms this correlation.

CONCLUSIONS

TRLFS and FTIR spectroscopy offer new opportunities to identify thin coatings of secondary U^{6+} -bearing phases on rock or mineral surfaces in a fingerprinting procedure. Becquerelite is identified by four fluorescence emission bands at 518.9, 535.6, 553.4, and 578.9 nm, and a characteristic fluorescence lifetime of $3.1 \pm 0.2 \mu\text{s}$. Swartzite is associated with six characteristic fluorescence emission bands at 472.3, 488.9, 509.0, 531.1, 554.7, and 578.9 nm, and a fluorescence lifetime of $59.4 \pm 0.1 \mu\text{s}$.

In addition, the FTIR spectrum of becquerelite is characterized by an intense and asymmetric stretching vibration ($\nu_3 \text{UO}_2^{2+}$ mode) band at 946 cm^{-1} ; it shows shoulders at approximately 925 and 902 cm^{-1} . The FTIR spectrum of swartzite is characterized by the $\nu_3 \text{UO}_2^{2+}$ mode of the uranyl cation at 898 cm^{-1} .

The spectroscopic information obtained is of fundamental importance in studies of the adsorption of the uranyl ion, in order to identify its coordination environment and the structure of unknown adsorbed species containing U^{6+} on mineral surfaces.

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