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Spectroscopic characterization of alkaline earth uranyl carbonates

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Abstract

A series of alkaline uranyl carbonates, $M[UO_2(CO_3)_3]\cdot nH_2O$ ($M = Mg_2$, Ca_2, Sr_2, Ba_2, Na_2Ca, and CaMg) was synthesized and characterized by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) after nitric acid digestion, X-ray powder diffraction (XRD), and thermal analysis (TGA/DTA). The molecular structure of these compounds was characterized by extended X-ray absorption fine-structure (EXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS). Crystalline $Ba_2[UO_2(CO_3)_3]\cdot 6H_2O$ was obtained for the first time. The EXAFS analysis showed that this compound consists of $(UO_2)(CO_3)_3$ clusters similar to the other alkaline earth uranyl carbonates. The average U–Ba distance is 3.90 ± 0.02 Å.Fluorescence wavelengths and life times were measured using time-resolved laser-induced fluorescence spectroscopy (TRLFS). The U–O bond distances determined by EXAFS, TRLFS, XPS, and Raman spectroscopy agree within the experimental uncertainties. The spectroscopic signatures observed could be useful for identifying uranyl carbonate species adsorbed on mineral surfaces.

Keywords: Uranium; Alkaline earth; Carbonate; Synthesis; Structure; Spectroscopy; EXAFS; TRLFS; XPS

1. Introduction

A number of alkaline earth uranyl carbonates have been found in nature, e.g., liebigite (CaUC), $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$, bayleyite (MgUC), $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$, andersonite (NaCaUC), $Na_2Ca[UO_2(CO_3)_3]\cdot 6H_2O$, swartzite (CaMgUC), $CaMg[UO_2(CO_3)_3]\cdot 12H_2O$, fontanite, $Ca[(UO_2)_3(CO_3)_2O_2]\cdot 6H_2O$, metazellerite, $Ca[UO_2(CO_3)_2]\cdot 3H_2O$, and zellerite, $Ca[UO_2(CO_3)_2]\cdot 5H_2O$ [1]. Since actinide carbonates exist over a wide range of environmental conditions [2], the last few years have seen a renewed interest in the study of uranyl carbonates in solid [3–6] and aqueous phases [7–9]. Uranyl carbonates are important for understanding the mobility of actinides in the environment. For example, recent studies of seepage waters of a mine tailing pile and mine waters of a uranium mine in Saxony, Germany, lead to the discovery of the important aqueous species $Ca_2UO_2(CO_3)_3$(aq.) [10,11]. In addition, uranyl minerals are found in soils contaminated by actinides, e.g., uranyl phosphate (meta-autonite) at the site of a former uranium processing plant at Fernald in Ohio, USA [12]. Uranyl minerals need to be considered also as important alteration phases of nuclear waste in a geological repository [13,14] or as coatings on mineral surfaces [15]. The identification of even minor amounts of such secondary uranium phases is a necessity for a better understanding of the uranium mobilization in the environment.

We report on the synthesis of the alkaline earth uranyl carbonates MgUC, CaUC, barium uranyl carbonate (BaUC), NaCaUC, and CaMgUC and their characterization by several spectroscopic techniques, i.e., time-resolved laser-induced fluorescence spectroscopy (TRLFS), extended X-ray absorption fine-structure (EXAFS) spectroscopy, and X-ray photoelectron spectroscopy (XPS). These spectroscopic techniques are non-destructive and sensitive to uranium(VI) in sample areas of a few μm^2 (TRLFS [16], micro X-ray absorption spectroscopy [17]), or allow the qualitative

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and quantitative analysis of surface layers with a thickness of a few nm (XPS [18]). The spectroscopic signatures of the alkaline earth uranyl carbonates reported here could be useful for identifying uranyl carbonate species adsorbed on mineral surfaces or formed as alteration products of nuclear waste.

2. Experimental

2.1. Synthesis of alkaline earth uranyl carbonates, $M[UO_2(CO_3)_3]\cdot nH_2O$

Many synthetic routes to alkaline earth uranyl carbonates are reported [19–23]. In this work, two methods—direct synthesis and metathesis reaction—were used for the synthesis of these compounds.

Direct synthesis: Alkaline earth uranyl carbonates were synthesized in aqueous solution by reacting stoichiometric amounts of uranyl nitrate, alkaline metal (in form of nitrate or chloride) and sodium hydrogen carbonate/sodium carbonate according to the following reaction:

$$\begin{aligned}&UO_2(NO_3)_2\cdot nH_2O + 2M(NO_3)_2\cdot nH_2O + 3Na_2CO_3\\&\quad\rightarrow M_2\left[UO_2(CO_3)_3\right]\cdot nH_2O + 6NaNO_3 + nH_2O\end{aligned}\tag{1}$$

(M = divalent cation).

Metathesis reaction: The preparation of the alkaline earth uranyl carbonates was based on the double exchange reaction between magnesium, ammonium, or sodium uranyl carbonate with the alkaline metal nitrate or chloride. The weaker cation in the uranyl carbonate was displaced by an alkaline earth metal according to the following reaction:

$$\begin{aligned}&(NH_4)_4UO_2(CO_3)_3 + 2M(NO_3)_2\cdot nH_2O\\&\quad\rightarrow M_2[UO_2(CO_3)_3]\cdot nH_2O + 4NH_4NO_3\end{aligned}\tag{2}$$

(M = divalent cation).

With these two methods, we were able to reproducibly synthesize the alkaline earth uranyl carbonates with high phase purity in relatively short time. Further details of the synthesis can be found in [24–26].

2.2. Chemical composition

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), whereas alkaline metal (Mg, Ca, Sr, Ba) and sodium contents were determined using a flame atomic absorption spectrometer (AAS, AAS 4100, Perkin Elmer, Überlingen, Germany). The H_2O and CO_2 contents of the air-dried samples were determined using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). These two techniques were performed using a thermoanalyzer (STA 92, Setaram, Lyon, France) with the following parameters: temperature range from 20 to 1000 °C with a heating rate of 10 °C/min, oxygen flow of 3 L/h, and sample mass of about 30 mg in an aluminum crucible. The buoyancy correction for the TGA was done by measuring a blank. The reference sample for DTA was Al_2O_3.

2.3. X-ray powder diffraction

The X-ray powder-diffraction of each crystalline phase was recorded with the Universal-Röntgen-Diffraktometer (URD 6, Freiberger Präzisionsmechanik, Freiberg, Germany) using CuK_α, ($\lambda = 0.1542$ nm) at 40 kV and 30 mA. Silicon powder was used as an external standard. The diffractometer was operated in Bragg–Brentano geometry in step-mode with a step width of 0.05°. The X-ray diffraction diagrams were recorded in the 2θ range from 5° to 60°. The Diffracplus Evaluation program (Siemens) v. 2.2 [27] was used for data collection and for reflection indexing and refining. The lattice spacing d and the lattice constants a, b, and c were calculated using the program Win-Metric [28] after peak fitting of a measurement with a silicon standard.

2.4. Time-resolved laser-induced fluorescence spectroscopy

The laser pulses from a Nd-YAG laser (model DIVA II, Thales Laser, USA) were applied to the solid samples of alkaline earth uranyl carbonates where the actual laser power was monitored with an optical power meter (model 1835C, Newport, USA) to allow for corrections due to fluctuations in the laser power. 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, USA). The fluorescence spectra were measured by a multichannel gate diode array (M 1475, EG&G) cooled to −30 °C. The spectra were collected with a controller (M 1471A, EG&G, USA). A more detailed description of the experimental setup can be found in [29]. The excitation wavelength was 266 nm. The spectra were recorded in the range from 400 to 600 nm with delay times from 0.1 to 160 μs after the application of the laser pulse. The gate time was 0.2 μs. The average laser power was 0.4 mJ. For every delay time, the fluorescence signal was averaged by sampling the single spectra over 100 laser shots. All functions (time controlling, device settings, recording of the spectra, data storage) of the spectrometer were computer controlled. The computer software GRAMS/386TM (Galactic Ind. Corp., USA) was used for the