One of Nature’s Puzzles Is Assembled: Analog of the Earth’s Most Complex Mineral, Ewingite, Synthesized in a Laboratory

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Abstract: Through the combination of low-temperature hydrothermal synthesis and room-temperature evaporation, a synthetic phase similar in composition and crystal structure to the Earth’s most complex mineral, ewingite, was obtained. The crystal structures of both natural and synthetic compounds are based on supertetrahedral uranyl-carbonate nanoclusters that are arranged according to the cubic body-centered lattice principle. The structure and composition of the uranyl carbonate nanocluster were refined using the data on synthetic material. Although the stability of natural ewingite is higher (according to visual observation and experimental studies), the synthetic phase can be regarded as a primary and/or metastable reaction product which further re-crystallizes into a more stable form under environmental conditions.

Keywords: uranyl; carbonate; ewingite; mineral; nanocluster; topology; crystal structure; structural complexity; X-ray diffraction

1. Introduction

It is well known that modern preparative chemistry emerged as a new field of science from mineralogical studies about 500 years ago. One of the founding fathers of this discipline was Georgius Agricola, who worked in the city of St. Joachimsthal (modern Jáchymov, Czech Republic) in the middle of the 16th century. This region of Ore Mountains, including Joachimsthal, has long been known for its unique geological and mineralogical treasures [1,2].

Georgius Agricola brought silver mining to a novel metallurgical level [3], whereas at the end of the 19th century, Pierre and Marie Curie discovered polonium and radium from the Joachimsthal uranium ores [4], and 50 years later the same uranium ores served as the basis for the creation of the USSR’s nuclear industry. Although uranium mining ceased in 1964, its remains in the Jáchymov ore district continue to provide scientists with exceptional and diverse mineralogical samples. Many new U-bearing minerals have been described in Jáchymov recently (e.g., see [5–12]), including one of the most amazing and structurally the most complex known mineral, ewingite, Mg₈Ca₈[(UO₂)₂₄O₄(OH)₁₂(CO₃)₃₀](H₂O)₁₃₈ [13]. Ewingite was recently found in samples from the abandoned Plavno mine in the Jáchymov ore district and has an unprecedented structure based on uranyl carbonate nanoclusters.
Ewingite is formed during the alteration processes of uranium ores (mainly uraninite, \( \text{UO}_2\)) upon contact with carbonate-enriched groundwater, although the precise conditions and mechanisms of its formation are still unknown.

Herein, we report the synthesis and characterization of the novel synthetic compound \( \text{Ca}_2\{(\text{UO}_2)_{24}\text{O}_{44}\text{(OH)}_{12}\text{(CO}_3\text{)}_{36}\}\text{(HCO}_3\text{)}_{34}\text{(H}_2\text{O)}_{88} \), which contains ewingite-like uranyl carbonate nanoclusters, thus linking preparative chemistry with descriptive mineralogy.

2. Materials and Methods

2.1. Synthesis

Caution: While isotopically depleted U was used in these experiments, precautions for handling radioactive materials should be followed.

An aqueous solution of 0.0725 g (0.14 mmol) of uranyl nitrate dissolved in 2 mL of deionized distilled water was heated on a hot plate at 70 °C for 4–5 min. Then, 0.074 g (0.7 mmol) of CaCl₂ and 0.095 g (1.0 mmol) of \((\text{NH}_4)_2\text{CO}_3\) were added to the hot solution, which was stirred until all solid dissolved. The resulting yellowish transparent solution, which yielded a pH of 7, was left to evaporate in a watch glass at room temperature. Crystals of the synthetic ewingite-like compound (SE) begin to form after 12–18 h as the first precipitate, mostly in the form of fine- or cryptocrystalline powders with rare individual dendritic aggregates (Figure 1a,b). Shortly thereafter, massive crystallization of calcite started, making it almost impossible to select pure SE. This process was slowed by reducing the temperature to 4–5 °C, which also yielded slightly larger dendritic aggregates with single crystalline dendrite tips separated by up to 10–20 µm (single findings up to 50 µm). The primary and relatively pure crystallization of SE was observed in a laboratory without intensive ventilation without intensive ventilation, without air conditioning system and without heaters, respectively.

![Figure 1](image_url). The onset of crystallization of the synthetic ewingite-like compound (SE) (a), a dendritic aggregate of SE surrounded by fine crystalline calcite powder (b), and an SEM image of SE crystals (c).

2.2. Chemical Composition

The chemical analysis of SE was carried out with a Hitachi FlexSEM 1000 (Tokyo, Japan) scanning electron microscope (Figure 1c) equipped with an EDS Xplore Contact 30 detector and Oxford AZtecLive STD (Oxford, UK) system of analysis. The accelerating voltage was 20 kV and beam current was 5 nA. Only Ca, U, C, and O were detected, with elements with atomic numbers higher than that of beryllium below detection limits. The following standards and X-ray lines were used: Ca—CaF₂, K₂O, U—UO₂, Mβ.

The chemical composition of SE is (wt.%, CO₂ and H₂O calculated based on structure): CaO 9.98, UO₂ 58.90, CO₂ 15.06, H₂O 16.19, total 100.13. The empirical formula based on 278 O apfu is \( \text{Ca}_{20.70}\text{U}_{24.07}\text{O}_{23}\text{(CO}_3\text{)}_{36}\text{(HCO}_3\text{)}_{34}\text{(H}_2\text{O)}_{88} \), or, taking into consideration the structural data, \( \text{Ca}_{20.70}\text{(H}_2\text{O)}_{6}\text{U}_{24.07}\text{O}_{23}\text{(CO}_3\text{)}_{36}\text{(HCO}_3\text{)}_{34}\text{(OH)}_{12}\text{(H}_2\text{O)}_{88} \) (Figure 1c). N, Na, and K were not detected, resulting in the assignment of hydronium cations \( \text{H}_3\text{O}^+ \) as counter-ions in the structure of SE.
2.3. X-ray Diffraction Studies

The crystal structure of SE was determined from a greenish-yellow translucent dendrite tip with the dimensions 52 × 23 × 21 μm³ using single-crystal X-ray diffraction data collected by a Bruker Kappa Apex II Duo diffractometer at room temperature (microfocused MoKα radiation; 50 kV/0.6 mA; frame width 0.5°; exposure time 360 s/frame; Madison, WI, USA). Diffraction data were processed in the CrysAlisPro [14] program. The crystal structure of SE was solved by the dual-space algorithm and refined using the SHELX [15,16] programs incorporated in the OLEX2 [17] program package. The crystal structure of SE is tetragonal (P-4n2; a = 24.6098(2), c = 24.6246(4) Å; V = 14,913.7(3) Å³; Z = 2; R1 = 0.060; CSD 2166564 [for cif see Supplementary Materials]). The final model included coordinates and anisotropic displacement parameters for all non-H atoms. H atoms were not localized. The crystal structure of SE was refined as a 2-component twin using [010/-100/001] matrix with a statistically equal contribution of components (0.514(14)/0.486(14)).

Fragments of SE manually selected from synthesis products were used for the collection of powder diffraction data with a Rigaku Ultima IV diffractometer (CoKα radiation; 40 kV/30 mA; θ–θ Bragg–Brentano geometry; PSD D-Tex Ultra detector; Tokyo, Japan). A Rigaku SHT-1500 chamber was employed for experiments with SE in air over the temperature range of 25–800 °C; a Pt strip (20 × 12 × 2 mm³) was used as the heating element and sample holder. The temperature steps varied from 5 to 20 °C depending on the temperature range. The heating rate was 2 °C/min. The collection time at each temperature step was about 30 min. The irreversibility of the observed phase transformations was verified by collecting PXRD data following cooling.

Several fragments of SE were ground in an agate mortar for PXRD data collection using a Rigaku Ultima IV powder X-ray diffractometer (CuKα radiation; 40 kV/30 mA; θ–θ Bragg–Brentano geometry; PSD D-Tex Ultra detector; Tokyo, Japan) equipped with a background-free Si-single crystal sample holder at room temperature.

2.4. Infrared Spectroscopy

The IR spectrum of SE was recorded on a Bruker Vertex 70 (Bremen, Germany) spectrometer via the Attenuated Total Reflection Method in the region 4000–500 cm⁻¹ (Figure 2). A MIRacle ATR accessory (Pike Technology; Fitchburg, WI, USA) with a Ge ATR crystal was used. IR spectroscopy is consistent with the structural data.

Figure 2. Powder infrared absorption spectrum of the SE.

Infrared bands in the region above 2500 cm⁻¹ (at 3590, 3420, 3230, 3130, 3000, 2950, 2900, 2890, 2830, 2730, and 2580 cm⁻¹) are attributed to the ν O–H stretching frequencies of structurally nonequivalent H₂O molecules forming the H-bonding network in the structure of SE. According to Libowitzky [18], the set of bands in this region corresponds to the approximate O–H···O hydrogen bond lengths ranging between 2.6 and 3.2 Å. A band
observed at 1645 cm\(^{-1}\) is attributed to the \(v_2 (\delta)\) bending vibrations of symmetrically distinct H\(_2\)O molecules. Bands in the region from 1570 to 1200 cm\(^{-1}\) (1570, 1525, 1487, 1445 and 1402 cm\(^{-1}\)) are assigned to \(v_3\) antisymmetric stretching vibrations of structurally nonequivalent CO\(_3\) planar groups. The splitting of the \(v_3\) bands indicates the bidentate bonding of carbonate groups to uranyl ions in the crystal structure. The weak band at 1065 cm\(^{-1}\) is assigned as \(v_1\) symmetric stretching vibrations of CO\(_3\) groups. The band caused by \(v_2 (\delta)\) out-of-plane bending vibrations of CO\(_3\) groups is at 833 cm\(^{-1}\). Note that the \(v_2 (\delta)\) CO\(_3\) bending vibrations may overlap with the \(v_1\) UO\(_2^{2+}\) symmetric stretching vibrations. Bands at 739, 711, 687, 671, and 665 are assigned to the \(v_4 (\delta)\) in-plane bending CO\(_3\) vibrations.

Two strong bands at 891 and 873 cm\(^{-1}\) are attributed to the \(v_3\) antisymmetric stretching modes of UO\(_2^{2+}\).

3. Results and Discussion

3.1. Structure Descriptions

There are six crystallographically independent U\(^{6+}\) cations in the structure of SE, each of which is strongly bonded to two O\(^{2-}\) atoms, forming approximately linear O\(^{2-}\)≡U\(^{6+}\)≡O\(^{2-}\) uranyl cations (Ur) with U\(^{6+}\)≡O\(^{2-}\) bond lengths ranging from 1.69(2) to 1.801(16) Å. The Ur1, Ur2, and Ur3 ions are equatorially coordinated by five oxygen atoms each, resulting in the formation of pentagonal bipyramids (U1−3−O\(_{eq}\) = 2.232(16)−2.443(17) Å), whereas the Ur4, Ur5, and Ur6 ions are coordinated by six oxygen atoms belonging to three carbonate groups, forming hexagonal bipyramids (U4−6−O\(_{eq}\) = 2.40(2)−2.458(18) Å). There are ten unique carbonate groups in the structure of SE, nine of which link to the equatorial edges of U-centered hexagonal bipyramids (C−O = 1.19(3)−1.35(4) Å), while the tenth group is not linked to U atoms, and due to the presence of one elongated and two short C−O bonds (1.47(4), 1.27(4) and 1.29(4) Å) is defined as an (HCO\(_3\))^− group.

There are two types of fundamental building units (FBU) in the structure of SE. FBU-1 consists of three Ur1−3 pentagonal bipyramids sharing common equatorial edges, with one \(\mu^3\)-O atom common to all three bipyramids, forming a trimeric unit (Figure 3a). The O atoms shared between two adjacent uranyl ions are hydroxyl groups, while the O atoms of the equatorial planes that do not bridge uranyl ions are from monodentate carbonate groups that link the FBU-1 and FBU-2 units. The FBU-2 unit is formed by the Ur4, Ur5, and Ur6 hexagonal bipyramids, in which each uranyl ion shares edges with three (CO\(_3\))^− triangular groups (Figure 3b) to form uranyl tricarbonate clusters (UTC) that are common U-bearing structural units in uranyl carbonates [19]. Four FBU-1 and twelve FBU-2 are arranged to form a complex uranyl carbonate [(UO\(_2\)]\(_{24}\)O\(_4\)(OH)\(_{12}\)(CO\(_3\)]\(_{44}\)-supertetrahedral nanocluster (Figure 3c,d). The cluster can be described as a combination of a tetrahedron and a cube, where the FBU-1 trimers correspond to faces of the tetrahedron, whereas two FBU-2 units delineate elongated faces of the cube (Figure 3e).

Isolated uranyl carbonate supertetrahedral nanoclusters in SE are separated by a network of Ca\(^{2+}\) cations and H\(_2\)O molecules, both of which also occur inside the cluster. Five of the eight Ca sites are fully occupied. The Ca−O bond lengths range from 2.09(3) to 2.717(17) Å. Disorder (site splitting) and partial occupancies occur for the H\(_2\)O sites. Calcium cations do not directly bridge between clusters. A complex H-bonding network involving interstitial H\(_2\)O molecules, H\(_3\)O\(^+\) ions, and (HCO\(_3\))^− groups link supertetrahedral nanoclusters into the crystal structure of SE.

There are several notable differences between the crystal structures of ewingite and SE. Ewingite contains both Ca and Mg, the latter of which does not occur in SE. Although tetragonal, the unit cell of ewingite is larger than SE (I\(_41/a\)cd; \(a = 35.142(2), c = 47.974(3)\) Å; \(V = 59.2458(8)\) Å\(^3\)) [13]. However, the arrangement of supertetrahedral nanoclusters in both structures is nearly identical and can be described as a body-centered cubic (α-Fe type) packing with the distances between the centers of clusters at ~21.3 Å (Figure 4). The structure symmetries are related through the following sub-/supergroup sequence: \(P-4n2 \rightarrow I-42d\) (\(a' = 2a, b' = 2b, c' = 2c\) ) \(\rightarrow I-41/a\)cd—which explains the eightfold difference.
in the unit-cell volume of ewingite compared to SE. Symmetry breaking in ewingite may be attributed to the distribution of Ca and Mg ions, as well as to the higher H2O content.

![Figure 3](image_url)

Figure 3. Fundamental building units (FBU) in the structure of SE (a,b), and their arrangement into a supertetrahedral nanocluster (c,d) that is similar to the combination of a tetrahedron and a cube (e). Legend: uranyl pentagonal bipyramids = yellow; uranyl hexagonal bipyramids = green; different coloring of Ur polyhedra is used for clarity; red = O atoms; grey = C atoms.

The most significant difference between the two structures is that supertetrahedral nanoclusters in the structure of ewingite are formed from three FBUs: four trimers of pentagonal bipyramids, six uranyl tricarbonate, and six uranyl bicarbonate moieties [13]. The structure of SE has 12 uranyl tricarbonate units. It cannot be excluded that, due to the low quality of the natural ewingite crystals studied previously, some atoms of carbonate groups were not located in the difference-Fourier maps.

The similarity of the structural architectures of both compounds is clearly seen from the comparison of their powder XRD patterns (Figure 5a,b), where the overlapping basal peaks correspond to the supertetrahedral nanocluster packing. It should be also noted that slight grinding in an agate mortar results in the reduction in the unit cell observed in the XRD pattern from the shift of the basal reflections, which are responsible for the general cluster arrangement, to the far angular region, while reflections responsible for more subtle structural interactions are extinct (Figure 5c).
Ewingite is the mineral with the most complex crystal structure known to date and possesses the highest amount of structural information observed in minerals. The theory of structural complexity was developed by S.V. Krivovichev [20–23] and successfully implemented in recent works [24–27]. Olds et al. proposed that the information content of ewingite is c.a. 23,000 bits/cell [13]. Our recent consideration of the disorder of sites and the H atom assignment indicate that the structural complexity of ewingite is likely in the range of 19,500–21,500 bits/cell, depending on the hydration state [19]. The information-based complexity parameters for ewingite and SE are given in Table 1. Although the hydration state of SE probably may also vary, the structural complexity of the synthetic compound is half that of ewingite at 9515.770 bits/cell. The contribution of factors such as the H-bonding system, interstitial substructure, and cluster stacking to the overall structural complexity [28] in both compounds is comparable, which points to the similarity of substructural units’ arrangement and their role in ewingite and SE. The most significant difference is the topological complexity of the cluster, which is attributed to the aforementioned absence of specific carbonate groups in the structural model of ewingite. The tendency for the com-

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**Figure 4.** Arrangement of supertetrahedral nanoclusters in the structures of SE (a) and ewingite (b), which is similar to the body-centered cubic (α-Fe type) packing (c). Interstitial ions and molecules are omitted for clarity; central nanocluster in the body-centered cubic packing is green-colored. Legend: U-centered polyhedra = yellow; red = O atoms; grey = C atoms.

**Figure 5.** PXRD patterns calculated from the structural data of the ewingite (a), SE (b), and pattern collected during the PXRD measurement of ground SE sample (c).

### 3.2. Structural Complexity Analysis

Ewingite is the mineral with the most complex crystal structure known to date and possesses the highest amount of structural information observed in minerals. The theory of structural complexity was developed by S.V. Krivovichev [20–23] and successfully implemented in recent works [24–27]. Olds et al. proposed that the information content of ewingite is c.a. 23,000 bits/cell [13]. Our recent consideration of the disorder of sites and the H atom assignment indicate that the structural complexity of ewingite is likely in the range of 19,500–21,500 bits/cell, depending on the hydration state [19]. The information-based complexity parameters for ewingite and SE are given in Table 1. Although the hydration state of SE probably may also vary, the structural complexity of the synthetic compound is half that of ewingite at 9515.770 bits/cell. The contribution of factors such as the H-bonding system, interstitial substructure, and cluster stacking to the overall structural complexity [28] in both compounds is comparable, which points to the similarity of substructural units’ arrangement and their role in ewingite and SE. The most significant difference is the topological complexity of the cluster, which is attributed to the aforementioned absence of specific carbonate groups in the structural model of ewingite. The tendency for the com-
plexity parameters of synthetic compounds to usually be lower than those of minerals with identical or genetically similar topologies of U-bearing complexes was recently described for uranyl sulfates [29,30] and uranyl selenites [31] and seems to be quite common in general. On the other hand, the complexity of a crystal structure contributes negatively to the configurational entropy of the crystalline phase [32], although metastable polymorphs are usually structurally simpler than their more thermodynamically stable counterparts [33,34].

Table 1. Structural complexity parameters for ewingite and SE.

| Complexes That Contribute to Structural Complexity [27] | Ewingite [18] | SE |
|-------------------------------------------------------|---------------|----|
|                                                       | \(v\), Atoms | \(I_{G,\text{total}}, \text{Bits/Cell} (I_G, \text{Bits/Atom})\) | Contribution, % | \(v\) | \(I_{G,\text{total}}, \text{Bits/Cell} (I_G, \text{Bits/Atom})\) | Contribution, % |
| Topological complexity of the cluster                  | 220           | 1271.820 (5.781) | 6.9 | 244 | 1447.100 (5.931) | 15.2 |
| Structural complexity of the cluster                   | 220           | 1271.820          | 0   | 244 | 1447.100          | 0   |
| Stacking of clusters                                   | 880           | 3813.886          | 20.8| 488 | 1506.180          | 15.8 |
| Interstitial structure                                 | 588           | 4531.056          | 24.7| 318 | 2499.190          | 26.3 |
| H-bonding                                              | 1040          | 8717.650          | 47.6| 484 | 4063.300          | 42.7 |
| Structural complexity of the entire structure          | 2508          | 18,335.988 (7.311)| 100 | 1290 | 9515.77 (7.377)  | 100  |

According to visual observation and experimental studies, in terms of their preservation, ewingite is more stable in air than SE, in which polycrystalline aggregates undergo degradation even with insignificant mechanical stress, which can be seen from the experimental PXRD pattern (Figure 5c). The indexation of the SE PXRD pattern by the Pawley method using the TOPAS software [35] resulted in the following unit cell: tetragonal; \(a = 23.12(1), c = 22.92(3) \text{ Å}\) (Figure 6a). The high-temperature PXRD experiment demonstrates that SE readily loses its crystallinity, and traces from the basal reflections, which correspond to the uranyl carbonate nanocluster packing, disappear entirely after 80 °C (Figure 6b). Later, starting at \(c.a.\ 420 ^\circ \text{C}\) under continuous heating, the \(\text{CaUO}_4\) (PDF 01-085-0577; ICDD PDF-2 Database, release 2019 [36]) phase crystallizes.

The recent findings relating to the unnamed phase, equivalent to a now-described synthetic compound, at several localities in nature (Jáchymov, Czech Republic; Annaberg, Germany; Red Canyon district, Colorado, USA) have documented that the SE occurred there without the presence of ewingite (unpublished observations of J.P.). Furthermore, the first chemical analyses of the natural material also suggested a large chemical variability (namely in the Ca:Mg ratio), while the single-crystal X-ray diffraction patterns are very similar and also similar to those of SE. Nevertheless, these findings require deeper study, which is beyond the scope of this paper.

Keeping in mind the similar architecture of ewingite and SE as well as findings relating to the novel natural phase, it can be assumed that the formation of a particular crystalline form is highly dependent on the chemical composition of ground waters. On the other hand, since ewingite is apparently more stable, it is plausible that the SE phase can be regarded as a primary and/or metastable reaction product which further re-crystallizes into a more stable form under environmental conditions.
Figure 6. PXRD patterns of SE as a function of temperature (25–800 °C) under heating in air (a) and indexation of the SE PXRD pattern (b).

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/ma15196643/s1: CSD 2166564: contains the supplementary crystallographic data for this paper.

Author Contributions: Conceptualization, O.S.T. and V.V.G.; Methodology, O.S.T., A.V.K., M.G.K. and V.V.G.; Investigation, O.S.T., I.V.K., A.V.K., M.G.K. and V.V.G.; Writing—Original Draft Preparation, I.V.K., J.P., S.V.K., P.C.B. and V.V.G.; Writing—Review and Editing, J.P., S.V.K., P.C.B. and V.V.G.; Visualization, I.V.K., A.V.K. and V.V.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Russian Science Foundation (no. 19-17-00038), and by the Czech Science Foundation (no. 20-11949S to J.P.).

Acknowledgments: The XRD and spectroscopy studies were performed at the X-ray Diffraction Centre of St. Petersburg State University.

Conflicts of Interest: The authors declare no conflict of interest.
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