

# The super-space approach to the structures of selected U<sup>6+</sup> minerals and compounds

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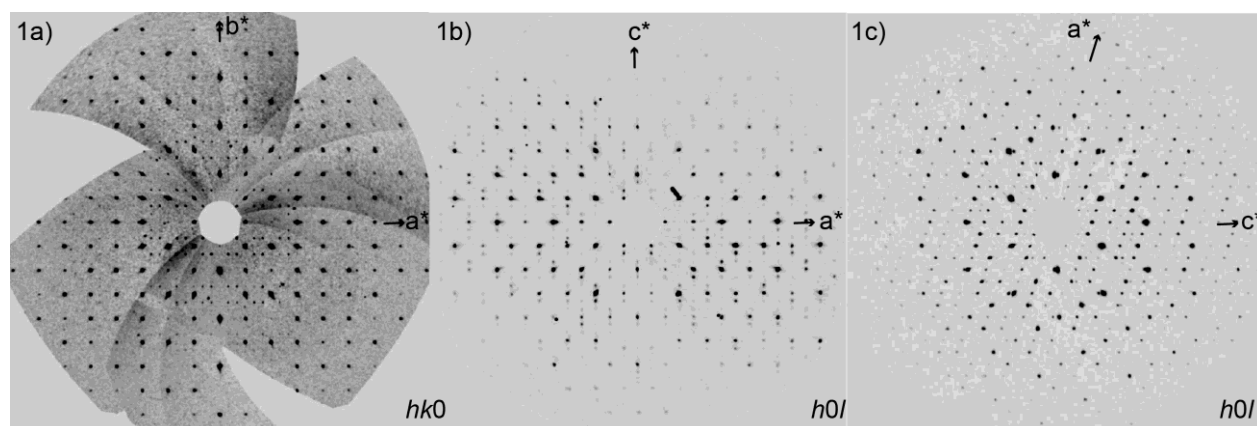
In Nature, uranium occurs in two most frequent valence states: as tetravalent and hexavalent. As hexavalent, it forms uranyl ion, UO<sub>2</sub><sup>2+</sup>, in the solid state a major constituent of a suit of minerals and compounds, whose structures are known for their remarkable compositional diversity and topological variability. Uranyl minerals are important alteration products of uraninite weathering, also referred to as oxidation–hydration weathering [1], and is of interest because of its analogy to the alteration of UO<sub>2+x</sub> in the spent nuclear fuel [2]. The recent review of the uranyl crystal-chemistry [3] summarizes the knowledge of 610 inorganic and 117 mineral well-refined structures. Among them, there has not been any mention neither about modulated and/or aperiodic structures so far. Nevertheless, quite recently several interesting mineral and inorganic structures that appear to be modulated have been discovered, and few of them have been described yet [4-6]. They are also of interest due to different reasons for the appearance of modulation in their structures.

Uranyl silicate mineral swamboite-(Nd), Nd<sub>0.333</sub>[(UO<sub>2</sub>)(SiO<sub>3</sub>OH)](H<sub>2</sub>O)<sub>2.41</sub>, was found to have a (3+3) commensurately modulated structure [4]. Its diffraction pattern is quite complicated due to presence of three modulation wave-vectors,  $q_1 = 1/3, 1/3, 0$ ;  $q_2 = -1/3, 1/3, 0$ ;  $q_3 = 1/2, 0, 1/2$  (Fig. 1a). It is monoclinic, the super-space group  $P2_1/m(a1, b1, g1)00(-a1, b1, g1)00(a2,0,g2)0s$ , with a unit-cell parameters  $a = 6.6560(3) \text{ \AA}$ ,  $b = 6.9881(5) \text{ \AA}$ ,  $c = 8.8059(6) \text{ \AA}$ ,  $\beta = 102.591(5)^\circ$  and  $V = 399.74(4) \text{ \AA}^3$ ,  $Z = 2$ . The structure of swamboite-(Nd) contains uranyl-silicate sheets of the uranophane topology and Nd atoms in the interlayer. The commensurate modulation originates from the distribution of the Nd sites in the structure and the consequent accommodation of the best geometry of uranyl-silicate sheets. In this case, we have highly charged cations, Nd<sup>3+</sup>, combined with structural uranyl-silicate sheet units of the –1 charge; this cause charge-frustrated settings which are relaxed by the strong modulation of the entire structure (occupational and positional).

Uranyl-oxide hydroxy-hydrate mineral shinkolobweite [5], Pb<sub>1.33</sub>[U<sup>5+</sup>(H<sub>2</sub>O)<sub>2</sub>(U<sup>6+</sup>O<sub>2</sub>)<sub>5</sub>O<sub>7.66</sub>(OH)<sub>2.34</sub>](H<sub>2</sub>O)<sub>5</sub>, possesses a (3+1) commensurately modulated structure with a single wave-vector  $q = 0, 1/3, 0$  (Fig. 1b). Shinkolobweite is orthorhombic, the super-space group  $Pnnm(0b0)000$ , with unit-cell parameters  $a = 14.4808(4) \text{ \AA}$ ,  $b = 7.0681(8) \text{ \AA}$ ,  $c = 11.9423(3) \text{ \AA}$ , and  $V = 1222.32(15) \text{ \AA}^3$ ,  $Z = 2$ . The structure is based upon the uranyl-oxide sheets of the  $\beta$ -U<sub>3</sub>O<sub>8</sub> topology and Pb atoms in the interlayer. The commensurate modulation appears due to occupational modulation of the Pb<sup>2+</sup> cations in the interlayer between hydrated-uranium-oxide-hydroxide sheets, and due to the long-range ordering of U<sup>5+</sup>/U<sup>6+</sup> at one of the cationic sites.

Baumoite is a rare uranyl molybdate [6], ~Ba<sub>0.75</sub>[(UO<sub>2</sub>)<sub>3</sub>O<sub>7</sub>Mo<sub>2</sub>(OH)<sub>5.5</sub>](H<sub>2</sub>O)<sub>~3.22</sub>, with a (3+1) incommensurately modulated structure. It is monoclinic,  $X2/m(a0g)0s$  with  $X=(0,1/2,0,1/2)$ , with unit-cell parameters  $a = 9.8840(13) \text{ \AA}$ ,  $b = 7.5406(2) \text{ \AA}$ ,  $c = 14.2276(13) \text{ \AA}$ ,  $\beta = 109.041(10)^\circ$  and  $V = 1002.4(2) \text{ \AA}^3$ ,  $Z = 2$ . Baumoite structure is based upon the uranyl-molybdate sheets of the unique topology, somewhat resembling the sheets in the synthetic Ag<sub>10</sub>[(UO<sub>2</sub>)<sub>8</sub>O<sub>8</sub>(Mo<sub>5</sub>O<sub>20</sub>)] [7], and Ba atoms in the interlayer. Incommensurate modulation, represented by the wave-vector  $q = 0.718, 0, 0.280$  (Fig. 1c), arises most probably from the distribution (long-range order) of the Ba atoms and consequent re-configuration of parts of the U-Mo sheets as well as H-bonds in an interlayer between them.

The intensity of satellite reflections is usually quite weak in case of the studied structure except of swamboite-(Nd), where the modulation effects are very strong. Nevertheless, the super-space approach enabled to refine all above-mentioned structures effectively; the refinements of the commensurately modulated structures of the two minerals in the supercells led to unstable refinements only. It is highly probable that other structures of uranyl minerals and compounds will turn out to be modulated, after all, namely due to use of high-sensitivity detectors for conventional structure analysis that can trap even weak-intensity satellite reflections.



**Figure 1.** Diffraction patterns (precession-like reconstructions from CCD frames) of the reciprocal lattice with apparent superstructural reflections of **a)** swamboite-(Nd), **b)** shinkolobweite, **c)** baumoite.

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