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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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CRYSTALLOGRAPHY

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On the Epitaxial Transformation $U_3O_8 \rightarrow UO_{2+x}$ in Nasturans

(Presented by Academician A. V. Shubnikov, 14 November 1963)

There is an assumption that nasturan was initially deposited in the form of U_3O_8, and then transformed into UO_{2+x} ([1,2]). Some nasturans of composition $UO_{2.6-2.7}$ are metamict, decomposed U_3O_8 ([1,3]). It has been established by electron microscopy ([4]) that, during reduction of acicular U_3O_8 crystals with rectilinear outlines, pseudomorphs of U_4O_9 are formed, and then UO_{2+x} after U_3O_8, having serrated outlines. The regular arrangement of the teeth indicates the existence of epitaxy phenomena during reduction:
$U_3O_8 \rightarrow U_4O_9 \rightarrow UO_{2+x}$. The possibility of an epitaxial transformation is also indirectly indicated by the inheritance of a number of properties of U_3O_8 (density, particle size) by the UO_{2+x} formed from it ([5]).

Fig. 1. Scheme of the orientational and dimensional correspondence of the uranium planar nets of U_3O_8 and UO_2. The uranium triangles are indicated by hatching. Each uranium atom has two oxygen atoms with height $\pm 0.5c$ (not shown); the other oxygen atoms have heights $\pm 0.17c$ according to Zachariasen (A) and $\pm 0.08c$ according to Andresen (B).

In the epitaxial transformation of U_3O_8 into UO_{2+x}, in accordance with the rule of orientational and dimensional correspondence ([6]), the UO_2 lattice will be oriented with the U_3O_8 lattice. Orientational and dimensional correspondence is achieved under the condition that the plane (111) of the cubic lattice of the forming UO_2 nuclei is oriented in the rhombic U_3O_8 lattice parallel to (001). In the (111) plane of the cubic lattice, the uranium atoms are located at the vertices and at the centers of the sides of an equilateral triangle, whose sides for a cell with $a_0 = 5.47$ Å are equal to 7.74 Å. The uranium atoms have an analogous arrangement (6 of 12 in the $U_{12}O_{32}$ cell) in the (001) plane of the U_3O_8 lattice,

Fig. 2. Schematic sketch of a nasturan spherulite (A) in a polished section etched with HNO3, and of individual zones of the spherulite at higher magnification (B-G).

Figure 2: Fig. 2. Schematic sketch of a nasturan spherulite (A) in a polished section etched with HNO3, and of individual zones of the spherulite at higher magnification (B-G).

where the base of the isosceles triangle is equal to ${}^{2}/_{3}b$ (b = 11.95 Å ([7])), i.e. 7.96 Å (Fig. 1), and at a temperature of 205-250°, which corresponds to the hydrothermal conditions of nasturan formation, is equal to 7.90 Å ([8]). The sides of the triangle are respectively 7.81 Å, and at 205°—7.84 Å. The greatest differences in the dimensions of the "uranium" triangles at 205° do not exceed 0.16 Å.

The uranium atoms of the unit cell $U_3O_8(U_{12}O_{32})$ form, in the (001) plane, two nets with coordinates $z = 1/4$ and $z = 3/4$ ([9]); consequently, the distance between the planar uranium nets is ${}^{1}/_{2}z = 2.07$ Å. The distance between the planar uranium nets in the UO_2 unit cell in the (111) plane is

3.13 Å. Thus, in the transition $U_3O_8 \rightarrow UO_{2+x}$, one of the two plane nets of U_3O_8 is used as the basis—apparently the densest one.

Epitaxy should manifest itself no less fully also in the transition $U_3O_8 \rightarrow U_4O_9$, since the uranium atoms in U_4O_9 and UO_2 are arranged analogously, and the sides of the "uranium" triangle of the cell with $a_0 = 5.44$ Å are equal to 7.69 Å. Epitaxy

Fig. 2. Schematic sketch of a nasturan spherulite (**A**) in a polished section etched with HNO_3, and of individual zones of the spherulite at higher magnification (**B-G**). **1** —hyperboloids of new spherulites; **2** —weakly etched zones of banded structure; the number under a zone indicates the number of bands; **3** —etched fibrous zones. **I-IV** (**B**) —structure of individual bands; the degree of etching is shown by dots; black —crystals of galena and coffinite; **G** —structure of fibers from an etched zone.

is also possible when an intermediate metastable tetragonal phase of the U_3O_7 type appears. In the transition, for example, $U_3O_8 \rightarrow \alpha\text{-}U_3O_7$ with the parameters of $\alpha\text{-}U_3O_7$ (at 210°) $a_0 = 5.47$ Å, $c_0 = 5.407$ Å [10], an isosceles uranium triangle is formed with sides of 7.69 Å and a base of 7.74 Å.

The concept of epitaxy agrees with known data on the structure and internal constitution of nasturan spherulites. Laue photographs of nasturan showed the existence of ordered spherulites and disordered segregations [11]. Interpretation of the Laue photograph of ordered nasturan spherulites made it possible to establish that the spherulites consist of UO_2 fibers elongated perpendicular to (111) [12]. On the basis of the existing inverse relationship between the habit of crystals and the form of elementary cells [13], from the dimensions of the elementary cell of U_3O_8, $a = 6.70$ Å, $b = 11.95$ Å, $c = 4.14$ Å [7], one may speak of elongation of the U_3O_8 fibers perpendicular to (001). In spherulites, the smallest parameter of the elementary cell coincides with the radius [14]. Thus, the orientation of UO_2 fibers in nasturan could have been caused by the primary orientation of U_3O_8 fibers.

The assumption of an epitaxial transformation $U_3O_8 \rightarrow UO_{2+x}$ in nasturans found full confirmation in the microscopic study of nasturans. Etching polished sections of nasturan with nitric acid revealed the granular structure of the fibers composing the spherulites.

Granular fibers consist of crystals of cubic habit intergrown at their vertices, which in section give quadrilaterals of the order of $1\,\mu$ in cross section. The central part (core) of the crystals is etched. In many fibers the etched cores merge, forming cellular structures. In most fibers even the partitions are not preserved, and the fibers are represented by hollow corrugated tubes (Fig. 2). Individual granular fibers are bent. In places several micron-sized crystals belonging to a group of adjoining fibers are united into small rhomboid blocks ($3–5\,\mu$ in cross section), isolated from one another, or forming short chains. The structure of the fibers indicates the secondary nature of the granularity of the spherulites.

Structural etching of nasturan reveals a complex periodic texture of the spherulites, caused by the alternation of etched and unetched zones (Fig. 2A–2). Granular fibers pass through all the concenters, but in the unetched zones, in the crystals making up the fibers, etching does not reveal cores, whereas in the etched zones, on the contrary, only shells remain of the crystals. The crystals composing the fibers of the spherulites in the etched zones consist of two uranium oxides differing in degree of reduction. The cores of the crystals in the fibers belong to relics of a still unknown intermediate uranium oxide. This shows that the epitaxial replacement $U_3O_8 \rightarrow UO_{2+x}$ was stepwise, and that reduction of the metastable oxide (U_2O_5 or U_3O_7) proceeded by centripetal diffusion of uranium from the crystal boundary.

The primary formation of U_3O_8 fibers oriented perpendicular to (001) agrees with the laws of structure [14] and growth [15] of spherulites. According to A. V. Shubnikov [15], the formation of spherulites from single and needlelike crystals occurs by splitting of growing crystals along the plane of best cleavage. In U_3O_8 crystals the cleavage is along (120) and (100), and the slip along (100) [16]; i.e., the formation of spherulites by splitting of U_3O_8 fibers oriented perpendicular to (001) is real. The primary formation of nasturan spherulites from UO_2 fibers perpendicular to (111) does not agree with the known regularities. It has been established [17] that UO_2 crystals have octahedral cleavage. In ordered nasturan spherulites the cleavage planes form spheres, i.e., they are arranged perpendicular to the radial directions of splitting.

Establishing epitaxy makes it possible not only to understand the nature of nasturans, but also to clearly distinguish nasturan from uraninite. Nasturan was initially deposited as a non-cubic mineral in the form of U_3O_8 (U_2O_5 is not excluded) and then passed stepwise (for ordered spherulites, epitaxially) into UO_{2+x}. Uraninite crystallized as a cubic mineral in the form of $U_4O_9(\rightarrow UO_{2+x})$ or UO_2.

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Note: Figure translations are in progress. See original paper for figures.