

Transmission Electron Microscopic Study of Reduced Ca_2UO_5

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Structural changes of Ca_2UO_5 during reduction in hydrogen were studied by transmission electron microscopy. It was shown that monoclinic Ca_2UO_5 changes into triclinic $\text{Ca}_4\text{U}_2\text{O}_9$. They are related, respectively, to the fluorite and the $\text{C-M}_2\text{O}_3$ structures, so that the product is a superstructure of the latter. Reduction occurs along the $(100)_t$ planes originating from the $(006)_m$ planes of the parent structure by diminishing the coordination number of the Ca cation from 7 to 6.

Introduction

It is known that the U-rich compounds in the $\text{CaO-UO}_2\text{-UO}_3$ system exchange oxygen with the surrounding atmosphere reversibly at higher temperatures (1-3), while the Ca-rich compounds do not change their stoichiometry up to the temperature of decomposition (3, 4). In the past little has been known about the behavior and stability of these compounds in a reducing atmosphere at higher temperatures. Recently, however, it has been shown that a change of structure is imposed when Ca_2UO_5 undergoes reduction to $\text{Ca}_2\text{UO}_{4.5}$ (5). In the present work, a transmission electron microscopic investigation was undertaken in order to elucidate this structural change. A similar study is being conducted on CaUO_4 , which exhibits a comparable change during reduction. These results will be published in a forthcoming paper.

Experimental

The materials used for the preparation of Ca_2UO_5 were Merck extra pure CaCO_3 and nuclear grade U_3O_8 . Appropriate proportions of powdered materials were mixed under alcohol, dried, and pressed into pellets. The samples were calcinated at 1520 K in oxygen for prolonged periods with intermittent cooling, crushing, mixing, and pressing to ensure homogeneity. X-ray analysis confirmed the presence of the pure Ca_2UO_5 phase only. Single crystals of Ca_2UO_5 were grown by melting 20% U_3O_8 , 10% CaO and 70% CaCl_2 (all in wt.%) at 1220 K and cooling them down to 970 K at a rate of 12 K/min. Single crystals up to 1 mm in diameter were leached out with cold water. Ca_2UO_5 was reduced in a hydrogen atmosphere at 870 K for at least 2 hr.

Specimens for the TEM study were prepared by crushing the pellet or small single

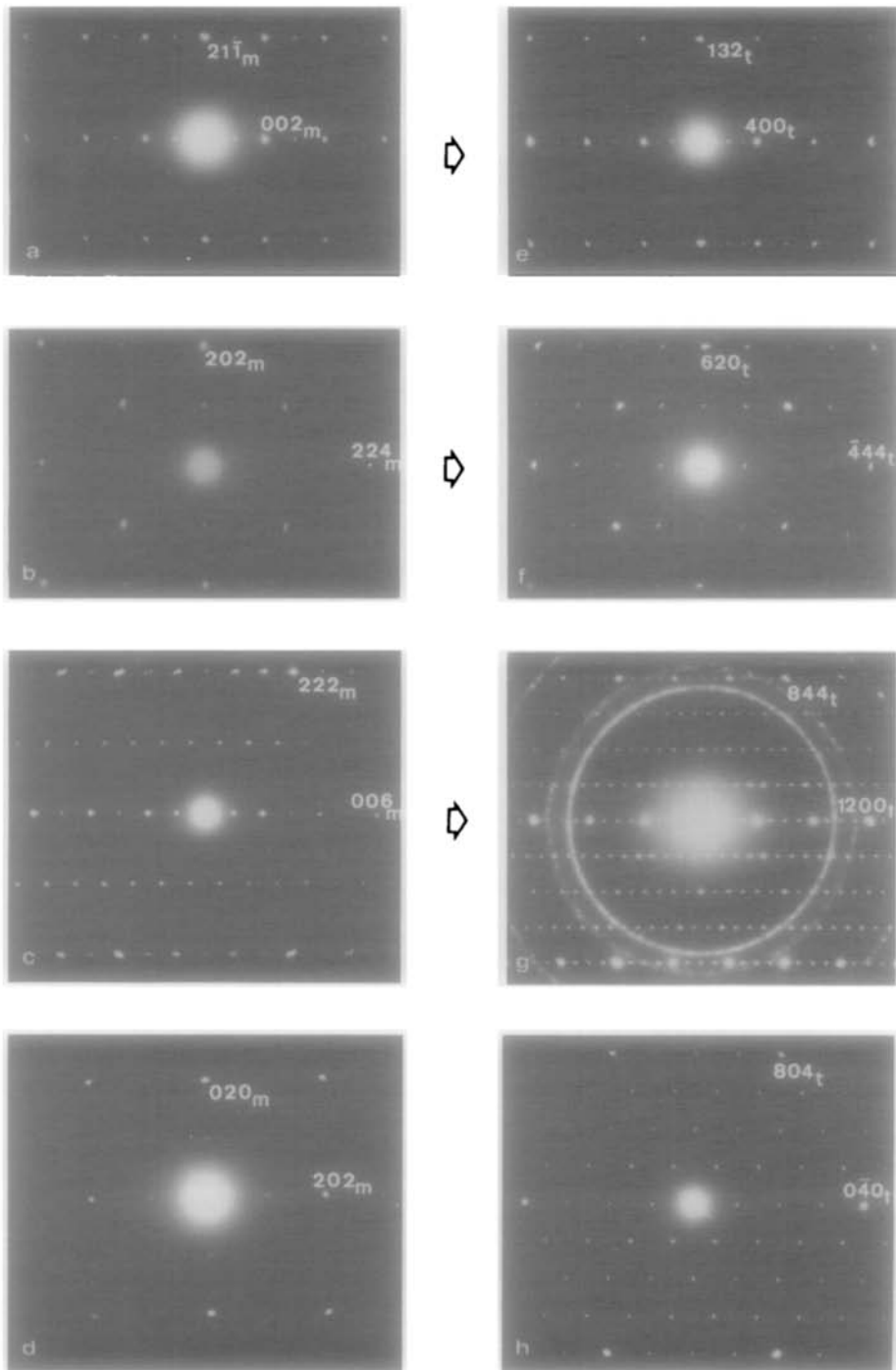


FIG. 1. a, b, c, d are the $\bar{1}20$, $[1\bar{1}\bar{1}]$, $[\bar{1}10]$, $[\bar{1}01]$ zones of the Ca_2UO_6 structure, respectively, and e, f, g, h are the $[023]$, $[\bar{1}34]$, $[011]$, $[\bar{1}02]$ zones of the product structure, respectively.

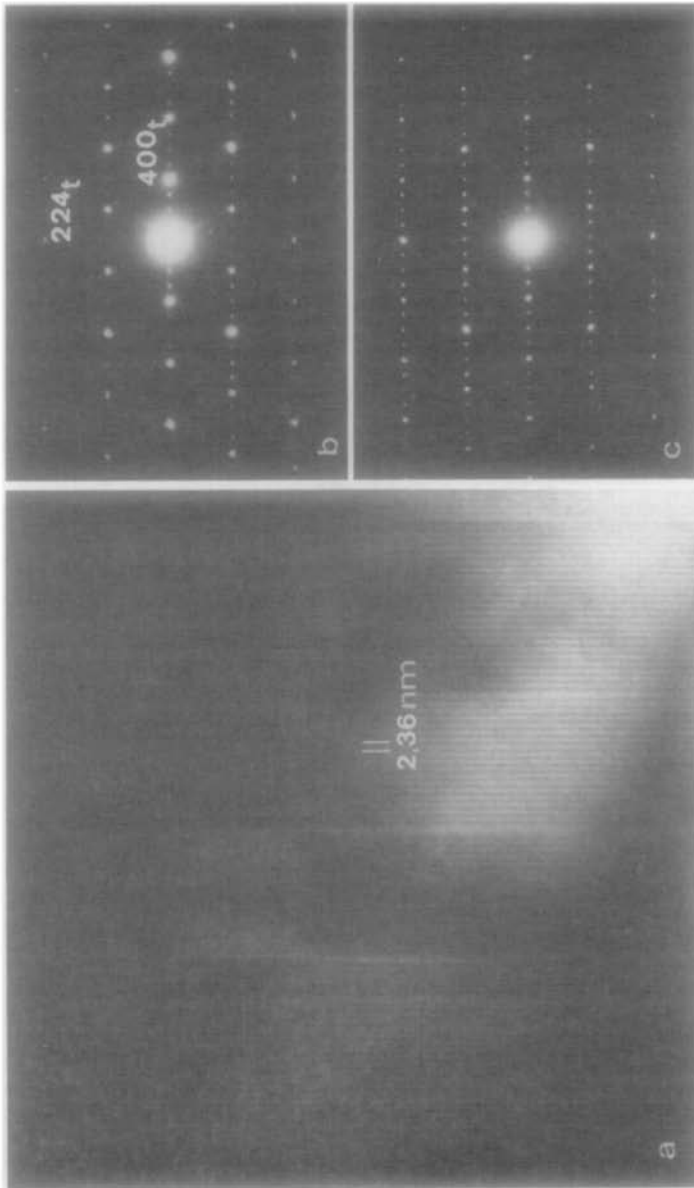


FIG. 2. Planar faults parallel to $(100)_m$ as seen edge on (a) and the corresponding diffraction patterns (b, c).

crystals into fine pieces which were dispersed onto holey carbon films. Sometimes a thin film of gold was evaporated over the specimen to calibrate the diffraction patterns internally.

Results and Discussion

Figures 1 show some prominent zones of Ca_2UO_5 (a–d), as well as those of the product structure (e–h). The corresponding zones are connected by arrows. The first easily noticeable feature caused by reduction is the appearance of new rows of reflections, as well as new reflections within the original rows. The intensities of the new reflections are comparable to the weak reflections of the original structure. The diffraction patterns of the resulting structure can be indexed on the basis of a triclinic structure, with approximate lattice parameters $a_t = 2.2980$ nm, $b_t = 0.9312$ nm, $c_t = 1.0712$ nm, $\alpha_t = 54.98^\circ$, $\beta_t = 76.54^\circ$ and $\gamma_t = 82.17^\circ$. The transition from the parent structure Ca_2UO_5 to the resulting superstructure is continuous, and the lattice undergoes a distortion during reduction which can be approximately described by the matrix

$$\begin{vmatrix} +0.04 & 0 & 0 \\ 0 & -0.03 & 0 \\ 0 & 0 & -0.01 \end{vmatrix} \quad (1)$$

with the principal axes along the normals to $(002)_m$, $(40\bar{2})_m$, and $(020)_m$, respectively. Furthermore, this distortion brings the angles as well as the interplanar spacings close to a fcc subcell with $a_c = 0.538$ nm, resembling that of UO_2 ($a_c = 0.547$ nm). This subcell can easily be recognized in all diffraction patterns (Figs. 1e–h).

In the early stage of reduction (~ 2 hr) planar defects were observed. Figure 2a represents a lattice image, taken with reflections along the central dense row in the corresponding diffraction pattern (Fig. 2b). Planar faults are present between regularly spaced interplanar distances with $d(100)_s = 2.36$ nm. For comparison, Fig. 2c shows the diffraction pattern of a specimen which was kept in the reducing atmosphere for 24 hr; the intensities of the additional reflections in this case are nearly equal to the intensities of the reflections originating from the parent structure. This means that prolonged treatment perfects the new structure.

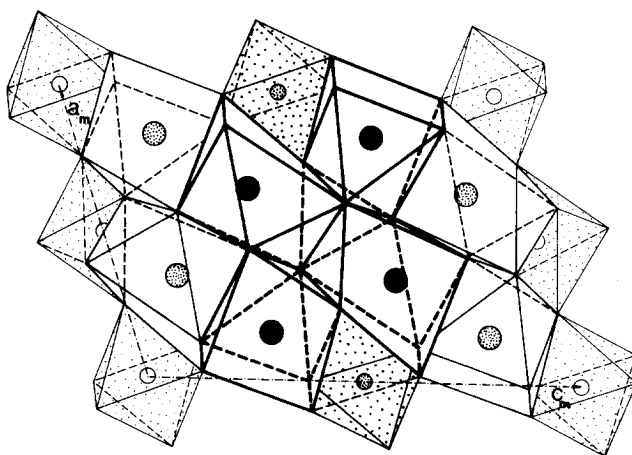


FIG. 3. The structure of Ca_2UO_5 . Large circles represent 7-coordinated Ca cations and small ones 6-coordinated U cations, centered in dotted octahedra. The oxygen ions are not shown. Empty circles are at $y = 0$, dotted at $y = \frac{1}{2}$, and black ones at $y = 1$, respectively.

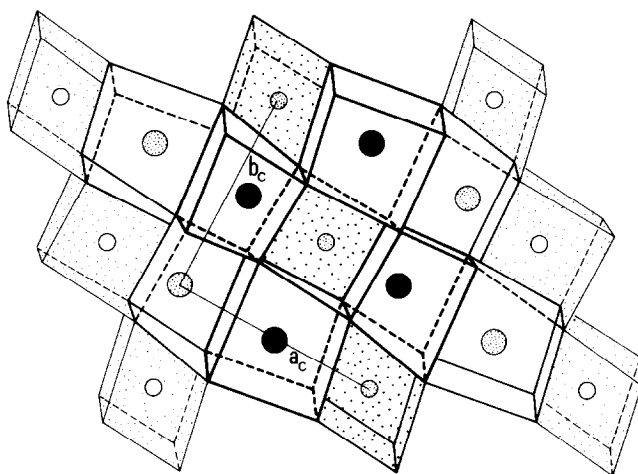


FIG. 4. The deformed fluorite structure, corresponding to the structure of Ca_2UO_5 shown in Fig. 3. Both the Ca and U cations are 8-coordinated deformed cubes. The circles and the lines have the same significance as in Fig. 3.

On the basis of the experimental evidence given above, it is obvious that the parent structure and the product one are closely related. The reduction takes place in such a way that the coordination of the cations in Ca_2UO_5 is changed in an ordered way. The structure of Ca_2UO_5 , which was described by Sawyer (6) and Loopstra and Rietveld (7), is shown in Fig. 3; the U cations are 6-coordinated and the Ca cations 7-coordinated. This structure can be considered as the first step of reduction of a deformed fluorite structure, shown in Fig. 4, where the cation coordination is 8. The reflections belonging to this subcell can easily be recognized in all the diffraction patterns. A further reduction changes both the U and Ca coordination into 6, resulting in the well-known cubic $\text{C-M}_2\text{O}_3$ (e.g., $(\text{Fe,Mn})_2\text{O}_3$ -bixbyite structure) with the unit cell edge a_c , twice that of UO_2 (8). This structure is shown in Fig. 5, and if the order between the U and Ca cations in Ca_2UO_5 is retained, the exact superstructure experimentally observed is obtained with a composition of $\text{Ca}_4\text{U}_2\text{O}_9$. This composition was confirmed by thermogravimetric analysis. The orientational relationship between the

$\text{C-M}_2\text{O}_3$ structure and the triclinic one, is shown in Fig. 5, and the transformation matrices between different structures are given below:

$$\begin{array}{ccc|ccc}
 & a_m & b_m & c_m & & a_c & b_c & c_c \\
 \hline
 a_t & 1 & 1 & 2 & a_m & -1 & 1 & 0 \\
 b_t & 1 & 1 & 0 & b_m & 0 & 0 & 1 \\
 c_t & 0 & 2 & 0 & c_m & 2 & 1 & 0 \\
 \hline
 & a_c & b_c & c_c & & a_c & b_c & c_c \\
 \hline
 a_t & 3 & 3 & 1 & a_{c'} & 2 & 0 & 0 \\
 b_t & -1 & 1 & 1 & b_{c'} & 0 & 2 & 0 \\
 c_t & 0 & 0 & 2 & c_{c'} & 0 & 0 & 2. \\
 \hline
 \end{array} \quad (2)$$

Finally, the planar defects were found to lie in the $(100)_t$ planes originating from $(001)_m$ planes. They can be explained as planes where the cation coordination of the old structure within the new one is retained. Obviously, reduction takes place preferentially along these planes and a certain time of annealing is needed to obtain the ordered reduced structure.

Conclusions

A new structure, with the composition

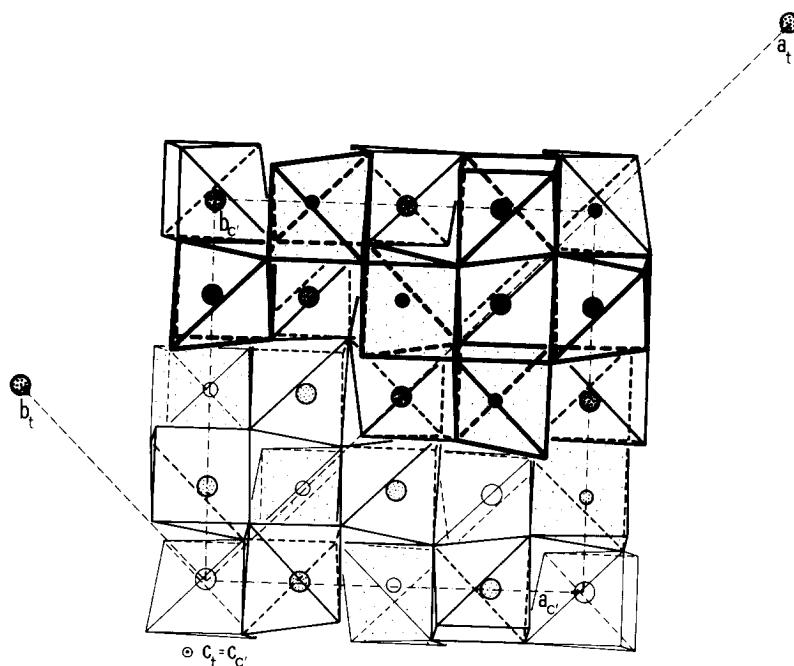


FIG. 5. A part of idealized structure of $\text{Ca}_4\text{U}_2\text{O}_9$. Only the unit cell of bixbyite is shown. Large and small circles, also corresponding to the undotted and dotted polyhedra, represent Ca and U cations, respectively. The orientational relationship between the structures of $\text{C}-\text{M}_2\text{O}_3$ (a_c , b_c , c_c) and the triclinic one (a_t , b_t , c_t) is also shown. The corners of the octahedra are deliberately shifted to show their shapes.

$\text{Ca}_4\text{U}_2\text{O}_9$ is formed during reduction of Ca_2UO_5 .

The new structure is based on the known $\text{C}-\text{M}_2\text{O}_3$ structure of bixbyite, where a superstructure is formed due to the ordering between the Ca and U cations.

Both the parent Ca_2UO_5 as well as the resulting $\text{Ca}_4\text{U}_2\text{O}_9$ structure are related to the fluorite structure.

Planar defects representing planes of nonreduced parent structure were observed in the early stage of reduction.

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