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Synthesis and Research of the Hydrated Oxide U(VI) with General Formula $\text{UO}_3 \cdot 2.25\text{H}_2\text{O}$

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A new method of synthesis of schoepite $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$ has been proposed in this work. Dehydration process of the synthesized compound has been studied, the state and role of H_2O in the structure has been established by means of high-temperature X-ray diffraction, IR spectroscopy and thermography. The transformation processes of schoepite in other forms of the hydrated oxide U(VI) have been investigated.

The individual crystalline phases of schoepite were synthesized by the two stages process. Earlier $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ was prepared and decomposed into UO_3 at 200°C . Thereafter this freshly obtained uranium (VI) oxide was hydrated by water vapor at 100°C .

An IR spectroscopic study was carried out in order to evaluate the functional group composition, the state of H_2O molecules and the state hydroxide groups in the structure of schoepite. The IR spectrum of $\text{UO}_3 \cdot 2.25\text{H}_2\text{O}$ contains three groups of absorption bands. Among these bands there are vibrations of H_2O molecules, UO-H group and uranyl bonds. In schoepite all H_2O molecules form two types of H-bonds. First type of bonds is formed by the interaction of H_2O molecules with each other. Interlayer H_2O molecules and hydroxide groups, which are included in the structure of layer, interact and form other type of H-bond. The average intensity peak of ν (UO-H) appears in the spectrum at 3356 cm^{-1} . Corresponding bands of δ (U-O-H) vibrations are intensive ones at 997 cm^{-1} .

For detailed determination of the schoepite structure and its resistance to high temperatures, a thermographic investigation has been carried out. Two H_2O molecules are removed from $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$ in one stage according to the first endotherm effect at $80\text{--}116^\circ\text{C}$. A new crystalline phase of meta-schoepite $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot (\text{H}_2\text{O})_{10}$ is formed as a result of these processes. This compound is stable at room temperature. The process of the meta-schoepite thermal decomposition occurs in one stage according to the second endotherm effect in the temperature range of $118\text{--}156^\circ\text{C}$. The dehydration product $(\text{UO}_2)_8\text{O}_2 \cdot (\text{OH})_{12}$ could not be obtained as the individual phase, because two H_2O molecules per formula unit of the compound are insufficiently for binding of the layers in the stable formation. At intermediate values of from 2 to 10 compound $(\text{UO}_2)_8 \cdot \text{O}_2(\text{OH})_{12} \cdot n\text{H}_2\text{O}$ should be regarded as a crystalline phase of variable composition, related to the class of solid solutions with different content of molecular water. The dehydration product with formula $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot (\text{UO}_3 \cdot \text{H}_2\text{O})$ isomerizes into α -modification of uranyl hydroxide $\alpha\text{-UO}_2(\text{OH})_2$. The condensation of hydroxide groups in $\alpha\text{-UO}_2(\text{OH})_2$ and formation of UO_3 occurs at the third endotherm effect at $289\text{--}361^\circ\text{C}$. This oxide decomposes to U_3O_8 at 500°C .

Thus schoepite, meta-schoepite and uranyl hydroxide contain the similar structure units such as H_2O molecules, uranyl and hydroxide groups. Different combination of these structural units is a reason of existence of a variety of chemical forms of $\text{UO}_3 \cdot n\text{H}_2\text{O}$.

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