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On the Cerium Dioxide — Uranium Dioxide System and „Uranium Cerium Blue"

ARNE MAGNÉLI and LARS KIHLBORG

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

Hofmann and Höschele [1] obtained dark blue, cubic crystals of a cerium uranium oxide by heating a mixture of cerous sulphate and uranyl sulphate with an excess of anhydrous magnesium chloride in a covered crucible at a high temperature. The composition, which varied somewhat for different preparations, was approximately $2CeO_2 \cdot UO_2$. The authors concluded that, owing to the intense colour of this product, which is quite different from those of the pure dioxides, this so-called uranium cerium blue should be considered as a definite chemical compound. By precipitating a solution of cerous nitrate and uranyl nitrate with excess ammonia the same authors obtained a yellow precipitate that turned deep blue after a while. The composition of this substance was approximately $2CeO_2 \cdot UO_2 \cdot 2H_2O$.

Cerium dioxide and uranium dioxide both crystallize with a lattice of fluorite type and the difference between their lattice constants is quite small. From this point of view, the occurrence in the cerium dioxide — uranium dioxide system of an intermediate phase did not seem very likely and we thus decided to study this matter. Intimate mixtures of the two oxides were heated in evacuated silica tubes at about 1000° C for several days. The products thus obtained were in the form of a dark blue or blue-black powder. They were investigated by taking X-ray powder photographs in Guinier focusing cameras (with monochromatized Cu-$K\alpha$ radiation), and in high angle Phragmén-Hägg focusing cameras (using Cu-K radiation).

For recrystallized cerium dioxide the lattice constant was found to be 5.412 ± 0.002 Å * in agreement with values recently reported by Harwood [2]

* All dimensions are referred to the wave lengths of Cu-$K\alpha_1$, $K\alpha_2$, and $K\beta$ radiation equal to 1.54050, 1.54434, and 1.39217 Å respectively.

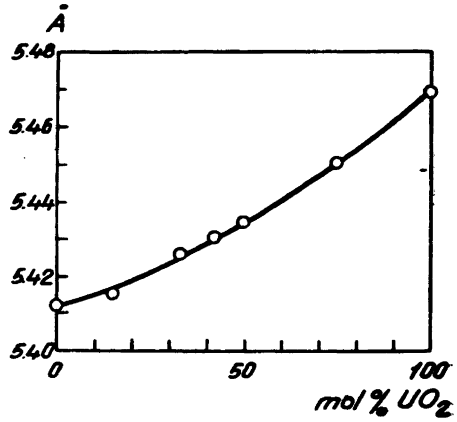

Fig. 1. Lattice constants for the system cerium dioxide — uranium dioxide.

(5.411 ± 0.002 Å) and Mc Cullough [3] (5.411 ± 0.001 Å). For uranium dioxide a value of a equal to 5.469 ± 0.002 Å was obtained. Rundle and his co-workers [4] have recently given an axial length of 5.4581 ± 0.0005 Å, however, without stating whether this value is expressed in kX or in true Å units. (If the former is the case this value will correspond to 5.4691 Å.)

The powder photographs showed the intermediate products to be homogeneous and to have the CaF_2-type lattice. No extra lines indicating a superstructure were visible even in amply exposed photographs. The lattice constants for the various preparations are represented in Fig. 1. Cerium dioxide and uranium dioxide evidently form a continuous series of solid solutions, as does cerium dioxide with thorium dioxide [5] and with praseodymium dioxide [3].

A sample of "uranium cerium blue" obtained by heating cerous nitrate and uranyl nitrate with anhydrous magnesium chloride gave powder photographs only containing the lines corresponding to a lattice of fluorite type with a equal to 5.44 Å. According to Fig. 1 this would indicate the composition of the specimen to be approximately $Ce_{0.4}U_{0.6}O_2$ (no chemical analysis was made). A preparation of "uranium cerium blue", that had been obtained from solution and dried at 120° C gave similar powder photographs but the lines were diffuse. After heating for six hours at about 950 °C in a stream of nitrogen the sample had lost all its water (~ 8 %) and recrystallized. The powder lines of the product appeared at unaltered positions but had now grown rather sharp. The lattice constant of 5.45 Å corresponds to the approximate composition $Ce_{0.25}U_{0.75}O_2$. It is thus obvious that these products of "uranium cerium blue" are not a definite chemical compound but are of variable composition and members of a continuous series of solid solutions $(Ce,U)O_2$ of fluorite type lattice.

SUMMARY

"Uranium cerium blue" is of variable composition and belongs to the continuous series of solid solutions formed by the isomorphous dioxides of uranium and cerium.

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