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X-RAY DIFFRACTION STUDY OF THE FORMATION OF SOLID SOLUTIONS IN URANIA-THORIA PREPARED BY AQUEOUS CHEMICAL PROCESSES

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The formation of solid solutions of (U, Th)O_2 was studied by X-ray diffraction on specimens prepared by a hydrolytical process and by co-precipitation. The uranium–thorium compounds obtained by the two processes were calcined, followed by reduction treatments in different conditions. The crystal structures of the products obtained after calcination of the powder blends prepared by both processes are given. The different stages of homogenization that occurred during reduction, were characterized by means of the relative peak positions. The activation energy for interdiffusion during the reduction process was found to be 42 kJ/mol.

1. Introduction

The oxides ThO_2 and UO_2 have crystallographic structures of the fluorite type, and a solid solution can be formed with these oxides [1,2]. The preparation of (U, Th)O_2 solid solutions from powder blends as nuclear fuel is technologically important. Many processes can be used to produce mixtures of uranium and thorium compounds, namely hydrolytical, co-precipitation, sol–gel and mechanical processes [3–6].

In previous work, the use of mechanical processes in attaining a solid solution formation of (U, Th)O_2 was described [5,7]. According to these papers, the temperature range of solid solution formation was 1400–1700°C. The activation energy of 318 kJ/mol. and 448 kJ/mol. was determined by Krishnan et al. [5]. Two stages of solid solution formation, surface diffusion in the early stage of the activation process and volume diffusion in the second stage were considered by the authors as the reasons for encountering two activation energies. An activation energy of 335 kJ/mol was also found by Tomasi et al. [7] for (U, Th)O_2 prepared from powder mixtures. It is also known that hydrolytical, co-precipitation and sol–gel processes require a sintering temperature range of 1000–1300°C for obtaining (U, Th)O_2 solid solutions [3,4,6], but the several stages of solid solution formation are not known.

The purpose of this work is:

(i) to characterize the crystal structures of the phases observed after calcination of uranium and thorium compounds prepared from the hydrolytical process and co-precipitation;
(ii) in the next step, to characterize the several stages of interdiffusion during reduction by means of the relative peak position, a method proposed by Delhez and Mittemeijer [8,9] and slightly modified in this paper; and
(iii) to determine the activation energy of the interdiffusion process during reduction.

2. Experimental

2.1. Specimens

2.1.1. Hydrolytical process

The process was based on a rapid solidification of droplets in hot oil [(95 ± 3)°C] from a rather concentrated uranyl nitrate solution and thorium nitrate solution containing urea and hexamethylenetetramine (solid "hexa"). This uranium–thorium feed solution was prepared by dissolving urea in a solution of uranylnitrate and thorium nitrate with addition of solid hexa at temperatures below +10°C. The microspheres, deep orange and transparent, were washed in hot water, dried and were mixed in an agate mortar so as to produce the yellow powder which will be referred to as hyd-samples. The hyd-samples were calcined at 800°C for two hours in air. The calcined samples, with dark colour, were aliquoted in 15 parts and were reduced as follows: at

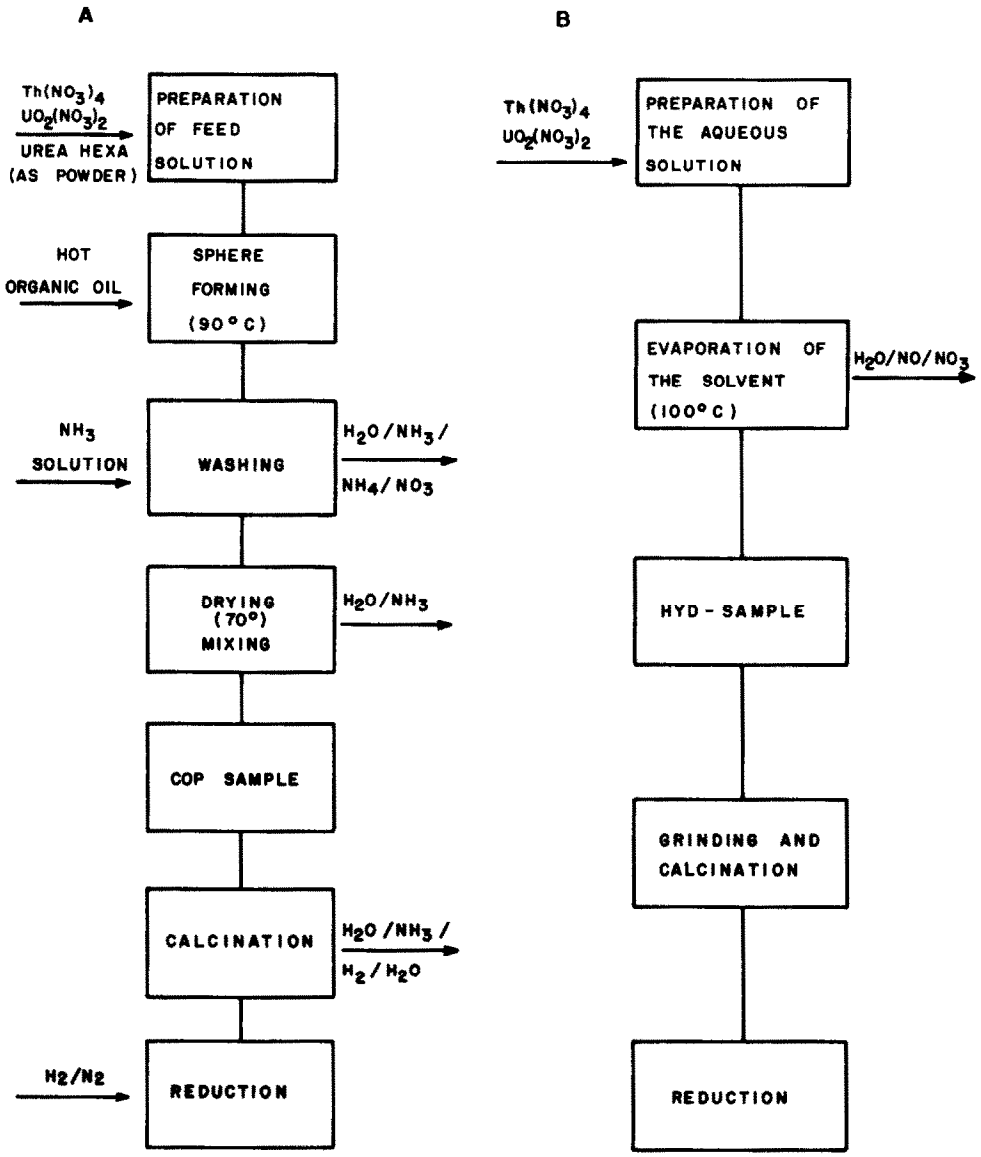

Fig. 1. The flowsheets showing the sample preparation steps from aqueous solutions: A, flowsheet of the hydrolytical method; B, flowsheet of the co-precipitation method.

600°C for 1, 2, 3, 4 and 5 h, at 700°C for 1, 2, 3, 4 and 5 h and at 800°C for 0.5, 1, 1.5, 2 and 2.5 h. Fig. 1A shows the flowsheet of the preparation process. It was performed in such a way as to produce hyd-samples with a uranium to thorium atomic ratio of 7 : 3.

2.1.2. Co-precipitation process

An aqueous solution of thorium nitrate and uranyl nitrate was prepared so as to form a mixture of uranium to thorium atomic ratio of 7 : 3. The solution was dried and the resulting product, cop-sample, was calcined at 800°C for two hours. Afterwards the sample was separated into 12 individual parts and each one was submitted to different reduction treatments as follows: temperatures of 570, 640 and 710°C for 1, 2, 5, 4 and 5.5 h. The steps for the specimen preparation are shown in the flowsheet of fig. 1B.

2.2. Diffractometry

A commercial goniometer equipped with a step-scanning system was used to perform the line profile measurements; the experimental setting of step scanning was 0.02° step and 2θ seconds fixed time counts. The (220) reflections were measured with $Cu_{K\beta}$ radiation because (a) it was a good compromise between high intensity and angular resolution and (b) no overlap occurred, (the use of $Cu_{K\alpha}$ results in the overlap of K_{α_1} and K_{α_2} radiations). The instrumental corrections by deconvolution of the line profiles were not effected since only the relative positions are of interest. The possible deviation of the relative peak positions due to the instrumental broadening was considered to be negligible in the present work.

The several stages of interdiffusion of uranium and thorium atoms during the solid solution formation of (U, Th)O_2 were characterized by measuring the relative peak position P_r for each reduction step. A slight modification of the definition of P_r, originally defined by Delhez and Mittemeijer [8,9], has been made as follows:

$$P_r = 1 - (P_1 - P_2)/(P_{01} - P_{02}), \quad (1)$$

where P_1 = actual peak position of ThO_2, P_2 = actual peak position of UO_2, P_{01} = initial peak position of ThO_2, P_{02} = initial peak position of UO_2. The P_r defined above is based on the peak position that can be experimentally determined and is different from the P_r defined in refs. [8,9] which is based on P_0 and P_∞ corresponding to the peak position at the start and the end of homogenization, respectively; P_∞ is calculated from the mean composition by use of Vegard's law. The relative peak position as defined in this paper is more advantageous than the original version from an experimental point of view. The calculated value of P_∞ is not required and $(P_1 - P_2)$ can be measured from a single experiment and is sensitive to deviation due to some disalignment of the instrument or the sample position. The mathematical equivalence between P_r defined in refs. [8,9] and defined in this work is easily demonstrated by application of a simple numerical relation, i.e, $A/B = C/D = (A + C)/(B + D)$, in Delhez's definition of P_r given by eq. (2):

$$P_r = (P_1 - P_{01})/(P_\infty - P_{01}) = (P_2 - P_{02})/(P_\infty - P_{02}) \quad (2)$$

2.3. Activation energy

According to Fick's second law, the basic process of diffusion of atoms yields a relationship between the continuous diffusion coefficient D and the average sum of the square of the individual jumps $\bar{x}^2$,

$$\bar{x}^2 = 2Dt, \quad (3)$$

where $(\bar{x}^2)^{1/2}$ also denotes the mean square displacement and gives the diffusion distance during time t [10].

When the proportionality between P_r^2 with respect to t is experimentally observed, i.e. $P_r^2 = Kt$, the process of solid solution formation can be assumed to be controlled by diffusion. In such a case, P_r^2 is also proportional to $\bar{x}^2$ and, according to eq. (3), the diffusion coefficient D is also proportional to K:

$$K = 2cD. \quad (4)$$

The Arrhenius equation can be represented in terms of K, as follows:

$$2cD = 2cD_0 \exp(-Q/RT),$$

$$K = K_0 \exp(-Q/RT). \quad (5)$$

The activation energy is obtained by means of eq. (5), from the Arrhenius plot K versus $(1/T)$.

3. Results and discussion

3.1. Calcination

Fig. 2 shows the diffraction pattern of cop-samples and hyd-samples, both calcined at 900°C for 2 h. In both patterns an overlap of the diffracted peaks of fluorite type and hexagonal structures was observed. In a more detailed examination, the following was verified (see table 1):

- the fluorite type peak positions correspond to a (U, Th)O_2 phase. According to Vegard's law, it can be considered as $(U_{0.7}, Th_{0.3})O_2$ phase;
- the remaining peaks correspond to a pseudo-hexagonal U_3O_8 structure. The pseudo-hexagonal U_3O_8 is stable at 500°C, whereas U_3O_8 has at environmental temperature a stable orthorhombic phase [11].

The stability of the pseudo-hexagonal phase at room temperature is probably due to the presence of thorium atoms in the U_3O_8 structure. The U_3O_8 dissolved in acids is transformed into different salts containing tetravalent and hexavalent uranium and therefore, it is sometimes represented by the unusual formula $2UO_3 \cdot UO_2$. Consequently, the pseudo-hexagonal phase, stable at room temperature, seems to be a solid solution which can be represented by $2UO_3 \cdot$ (U, Th)O_2 or (U, Th)$_3O_8$.

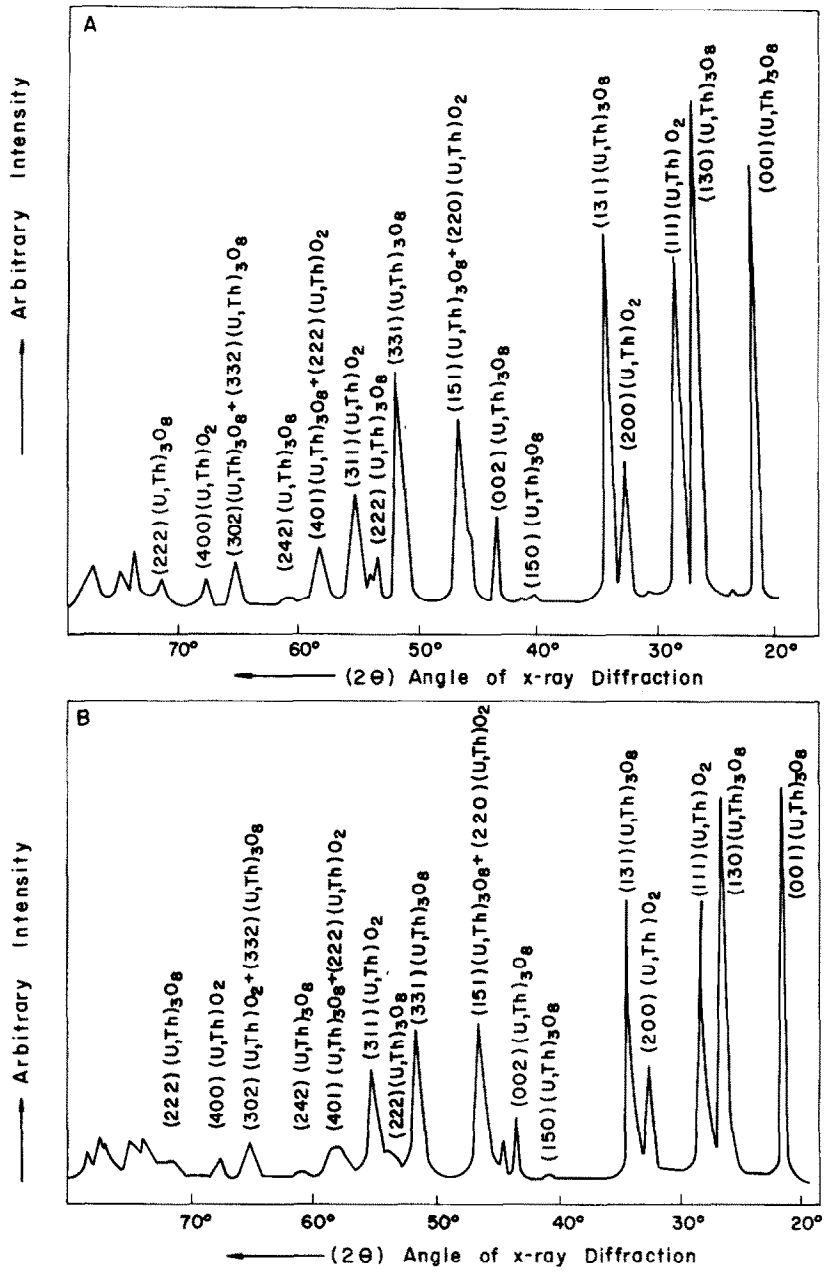

Fig. 2. Diffraction pattern of a calcined specimen prepared by: A, hydrolytical process; B, co-precipitation process.

3.2. Reduction

In the very early stage of reduction, the transformation of the pseudo-hexagonal phase into the fluorite type phase was observed. In the corresponding X-ray diffraction patterns, the disappearance of the pseudo-hexagonal peaks was observed followed by the appearance of a cubic phase, very near to the already existing fluorite type phase by formation of doublets. Fig. 3, for instance, shows the (220) line profiles from a reduced hyd-sample and cop-sample, respectively, at 700°C for 1 h and 570°C for 4 h.

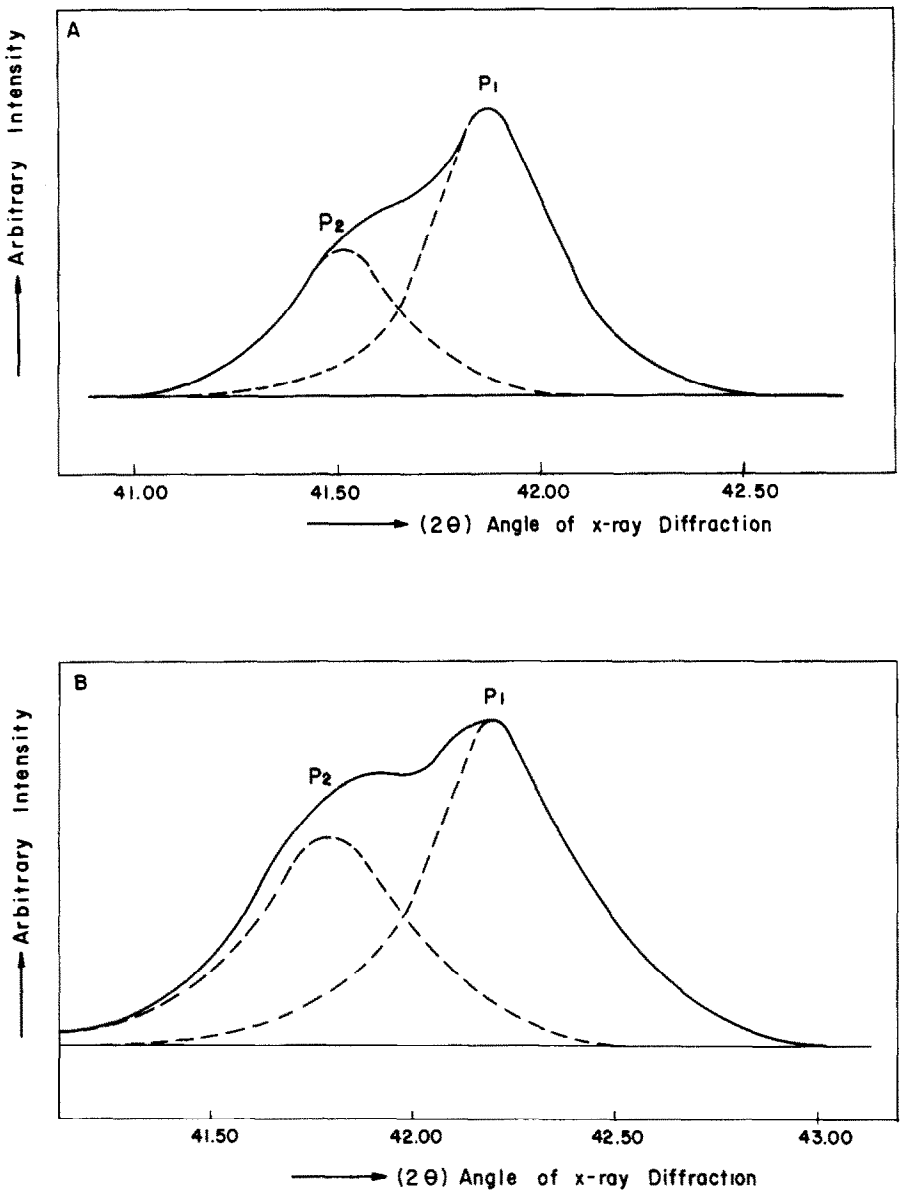

Fig. 3. (220) line diffraction profile at intermediate stage of solid solution formation: A, hyd-sample (reduced at 700°C by 1 h); B, cop-sample (reduced at 570°C by 4 h).

In fig. 4, the P_r^2 versus reduction time is plotted which shows a high degree of solid solution attained in a relatively short time. For instance, in fig. 3, a value of P_r around 0.59 was found for both reduced cop-sample and hyd-sample. The Arrhenius plot, derived from eq. (5), is presented in fig. 5. The activation energy of (42 ± 4) kJ/mol. was determined for both hyd- and cop-samples which is somewhat lower than those found in the literature for the mechanical process [5,7]. The cause of this low activation energy may lie at the beginning of the preparation of the specimens. After preparation of the uranium and thorium base solution, either by the hydrolytical process or by the co-precipitation process, the dissociation of uranium and thorium atoms has occurred shortening the mean path between them. Consequently, partially formed solid solutions

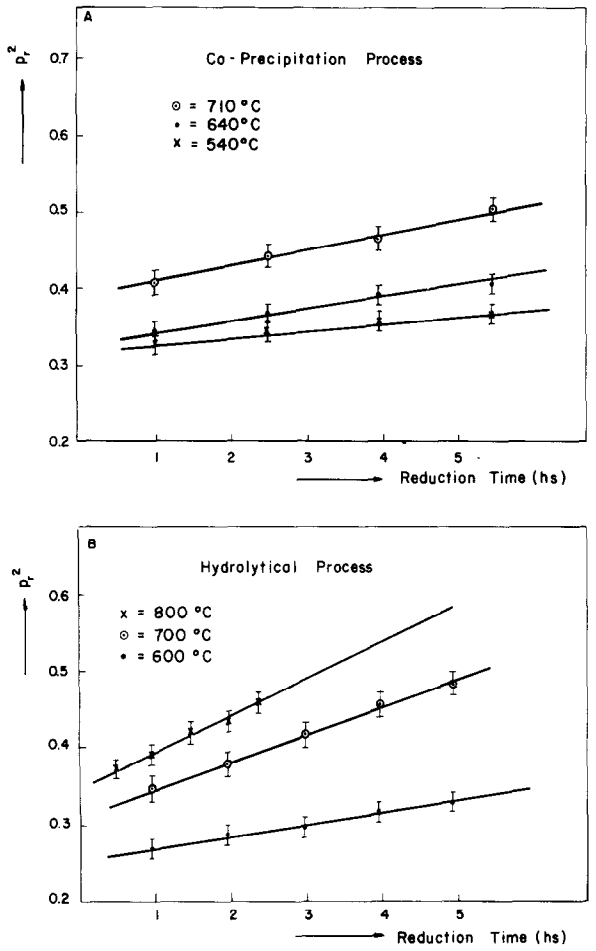

Fig. 4. The observed variation of the relative peak position as a function of the reduction time for both processes.

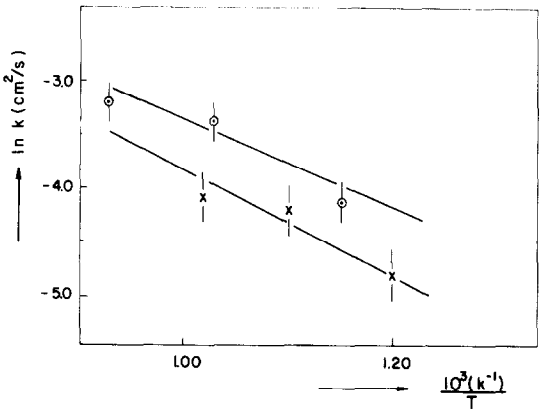

Fig. 5. Arrhenius plot for (U, Th)O_2 diffusional homogenization during the reduction process.

Conclusively, the steps of solid solution formation, observed in this work, are explained in the following way:

$$35\%\ \text{of}\ Th(NO_3)aq + 65\%\ \text{of}\ UO_2(NO_3)_2\ aq,$$
$$\xrightarrow{\text{calcination}} x\%\ \text{of}\ (U_{0.7}, Th_{0.3})O_2\ \text{(fluorite type)}$$
$$+(1-x)\%\ \text{of}\ 2UO_3 \cdot (U_{1-z}, Th_z)O_2\ \text{(hexagonal)},$$
$$\xrightarrow{\text{reduction}} (U_{0.7}, Th_{0.3})O_2.$$

Finally, it has to be mentioned that a similar study of solid solution formation was made in hyd-specimens prepared with an atomic ratio Th/U = 1/9, 2/8, 4/6 and 5/5. Since the kinetic behaviour was almost the same for any composition, only the study on hyd-specimens prepared with composition Th/U = 3/7 was described.

((U, Th)O_2 + (U, Th)$_3O_8$) were soon observed after calcination, and a high degree of solid solution (U, Th)O_2 was obtained during the reduction by means of a short range diffusion mechanism.

Acknowledgments

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Table 1
Lattice parameter and crystallographic structure after the calcination of the powders

Sample	Composition	Structure	Lattice parameter (Å)
			$a_0 = 6.83 \pm 0.04$
Hyd-sample	U_3O_8	pseudo-hexagonal	$b_0 = a_0\sqrt{3}$
			$c_0 = 4.14 \pm 0.06$
	ThO_2	f.c.c.	$a_0 = 5.51 \pm 0.02$
			$a_0 = 6.81 \pm 0.04$
Cop-sample	U_3O_8	pseudo-hexagonal	$b_0 = a_0\sqrt{3}$
			$c_0 = 4.14 \pm 0.06$
	ThO_2	f.c.c	$a_0 = 5.52 \pm 0.02$

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