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Original Article

Study of the elaboration of U_3O_8 by the Modified Direct Denitration process (MDD)

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ABSTRACT

In the nuclear industry, uranium trioxide (UO_3) is considered an intermediate in the preparation of uranium metal or uranium dioxide (UO_2), which are the two most widely used nuclear fuels. Several processes have been described for transforming solutions of uranyl nitrate $UO_2(NO_3)_2$ into uranium trioxide. Among these processes, Modified Direct Denitration (MDD) has been implemented to prepare Uranium trioxide with high reactivity. This process consists of adding ammonium nitrate to a pure uranyl nitrate solution to form the double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ which decomposes by calcination to produce a UO_3 powder. The objective of this work is to study, first, the thermal decomposition of double salt $(NH_4)_2UO_2(NO_3)4.2H_2O$ in nitrogen atmosphere by thermogravimetry in order to determine the formation temperatures of the different phases and second, the determination of the optimal parameters (time and temperature) to prepare stable triuranium octoxide (U_3O_8) using muffle furnace. As results, the MDD product obtained is an orange colored and free flowing UO_3 powder, having a surface area in the target range [5-12 m^2/g]. In addition, by calcination of UO_3 powder at 650°C for one hour, U_3O_8 oxide is obtained. The identification of the latter by the O/U ratio gave a value of 2.65, which is in the range [2.6-2.66]. This suggests that the oxide produced under these conditions is β-U_3O_8.

1. Introduction

Uranium trioxide has a great many uses. One of the most important applications is as the starting material for the production of uranium dioxide; for this purpose, uranium trioxide is transformed in triuranium octoxide and the otoxide is then reduced with hydrogen to uranium dioxide. uranium trioxide is frequently obtained by concentrating and calcining aqueous uranyl nitrate solutions.

Various methods are described to transform uranyl nitrate solutions [$UO_2(NO_3)_2$] into uranium trioxide UO_3 [1-4]. The process currently used to prepare UO_3, because it is simple to apply, is the direct thermal denitration of uranyl nitrate. The thermal decomposition of the uranyl nitrate in solution is carried out in a chemical reactor and a simple heat supply to the initial solution makes it possible to obtain the oxide UO_3. However, this method has certain disadvantages which limit its use [5]. Indeed, the massive character of the uranium trioxide (UO_3) poses a particular problem in batch mode. Under these conditions, recovery may be incomplete because of the difficulty in recovering the product that forms on the walls of the chemical reactor. Moreover, the product obtained has poor properties, that is to say an oxide generally agglomerated and composed of coarse grains with a relatively low specific surface area; which also offers a low reactivity in the subsequent physical or chemical transformation steps [6].

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In order to remedy these problems, the modified direct denitration process (MDD) has been developed. The MDD process was developed at the Oak Ridge National Laboratory (ORNL) to allow the use of simple denitration equipment and procedures as well as to prepare a UO_2 product with good ceramic properties [7]. The latter involves the thermal decomposition of the double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$, which is prepared from a solution of $UO_2(NO_3)_2$ and ammonium nitrate (NH_4NO_3). The final product obtained is a fine UO_3 powder, with a fairly high specific surface area, which gives it the reactivity necessary to be transformed into pellet. The aim of this work is to:

- determine the optimal molar ratio (NH_4^+/U) to obtain the double salt $(NH_4)_2UO_2(NO_3)_4\ _2H_2O$.
- study the thermal decomposition of double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ in nitrogen atmosphere by thermogravimetry in order to determine the formation temperatures of the different phases.
- Optimise parameters conditions (time and temperature) to prepare stable triuranium octoxide (U_3O_8) using muffle furnace.

2. Materials and Methods

2.1 . *Chemicals*

All chemicals and reagents used in this study were of analytical quality. Phosphoric acid (H_3PO_4, 85 %) and nitric acid (HNO_3) were purchased from Panreac. Ammonium nitrite (NH_4NO_3, 85%) was obtained from BDH, iron (II) ammonium sulfate was obtained from Fluka and the uranyl nitrate solution, which contains 330 g/L, was provided to us by the Uranium Purification Department of Nuclear Research Center of Draria.

2.2 . *Instrumentation*

Several instruments were used throughout the study namely muffle furnace (KR 260E, Heraeus), Micromeritics ASAP200/ 2010 surface area analyzer, thermogravimetric Analyzer (Labsys^{TM} TG-DTA12, SETARAM). Absorbance measurements were performed on a spectrophotometer SAFS monaco UVmc^1. The quartz cells used were l cm path length. Reagent blank (1M phosphoric acid) was used to adjust the base and numerical absorbance values before each run.

2.3 . *Experimental*

The samples of the double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ were prepared by mixing uranyl nitrate with ammonium nitrate by varying the molar ratio (NH_4^+/U) between 1.5 and 3 (table 1). The solutions obtained are then evaporated in the muffle furnace at about 50 °C. The six samples of double salt dihydrate obtained during the previous step are introduced into the muffle furnace, then heated according to the program below (fig 1and 2):

- Evaporation of the solution at 90 ° C with a heating rate of 1.5°C/min and maintaining this temperature for 90 minutes;
- Heating at a temperature of 170°C with heating rate of 4°C/min and maintaining this temperature for 60 minutes;
- Heating at a temperature of 300°C with heating rate of 4°C/min and maintaining this temperature for 90 minutes.

At the end of the heating program, the uranium trioxide elaborated was subjected to heat treatment at a temperature of 650°C during 60 and 120 minutes, in air atmosphere to U_3O_8.

The thermogravimetric analysis and differential thermal analysis were carried out on the double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ prepared with the ratio (NH_4^+/U) equal to 2.0 using a Labsys TM TG-DTA12 SETARAM Thermogravimetric Analyzer. Experiment was realized at a heating rate of 5 °C/min from 25 to 700 °C under nitrogen, using a sample mass 34.6 mg.

Table 1: Samples of $(NH_4)_2UO_2(NO_3)_4.2H_2O$ prepared with different NH_4^+/U molar ratio.

samples	NH_4^+/U Molar ratios
01	0
02	1.5
03	2.0
04	2.2
05	2.5
06	3.0

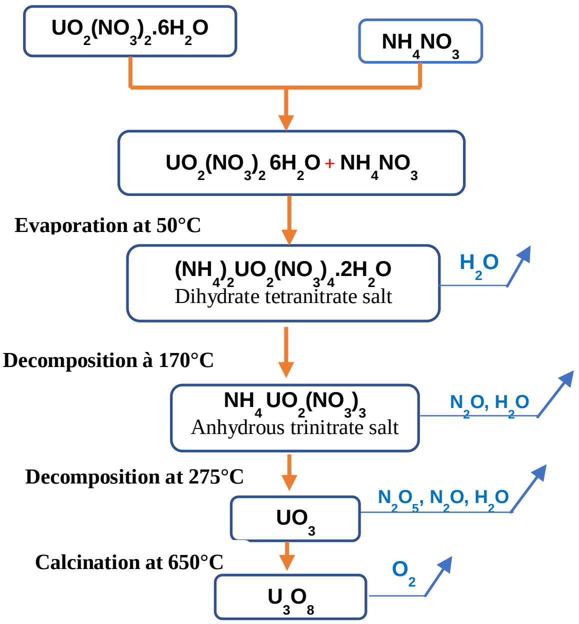

Fig 1. flowsheet of elaboration of U_3O_8 by the MDD process

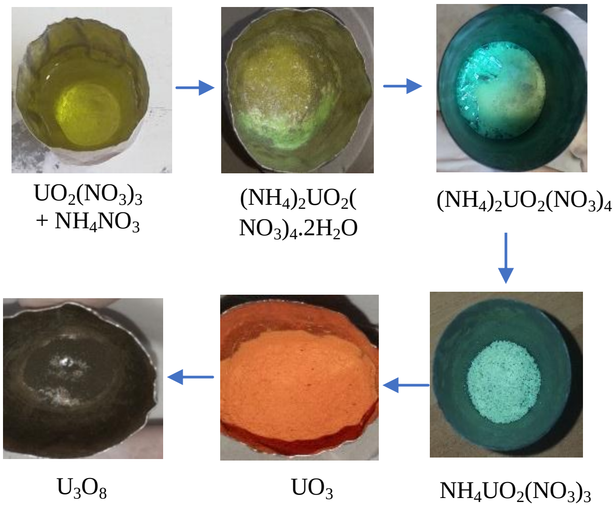

Fig 2. Images of different oxides prepared by the MDD process.

2.4 . *Identification of uranium oxides*

All the oxides obtained by calcination in muffle furnace are identified by determining their O/U ratios with the spectrophotometric method [8]. Since the degree of hyperstoechiometry can be directly related to the concentration of U(VI), the estimation of U(VI) as well as the total uranium allows the exact determination of the composition of the oxide. The O/U ratio was defined:

$$O/U = 2 + \frac{AU(T) - AU(IV)}{AU(T)} \quad (1)$$

Where AU(total) is absorbance of uranium (IV) and AU (IV) absorbance of uranium (VI).

2.5 . ***Dissolution of uranium oxides***

To obtain a reliable value for the O/U ratio of U_3O_8 powder, the oxidized state of the uranium oxide must remain unchanged during the dissolving process. For this purpose, we have carried out the dissolution under inert atmosphere (figure 3). A weighed amount (250-300 mg) of the of dried U_3O_8 powder was dissolved under nitrogen atmosphere in 25 ml of 1M phosphoric acid (H_3PO_4) at 150 °C. After dissolving of the U_3O_8 powder, the solution was cooled to room temperature under nitrogen atmosphere. Two samples of the dissolved uranium oxide solution (5 ml) were introduced in two test tubes, to which we added 1 ml of distilled water (H_2O) to the first sample and 1 ml of 1M of iron (II) ammonium sulfate $(NH_4)_2Fe(SO_4)_2.6H_2O$ to the second sample in order to reduce uranium (VI) in a H_3PO_4 solution to uranium (IV). Then, the absorbances were recorded immediately at 663 nm.

Fig 3. Experimental device used for dissolving of uranium oxides under inert atmosphere.

3. Results and Discussion

3.1 . *Double salt thermal decomposition*

Experiments carried out by mixing pure uranyl nitrate with ammonium nitrate at different NH_4^+/U molar ratios have shown the formation of solids (salts) at different evaporation times. In addition, all the solids obtained after calcination at 300°C are massive but friable (fig 4.a), with the exception of the solid obtained with the NH_4^+/U ratio equal to 1.5 which is not friable (fig 4.b).

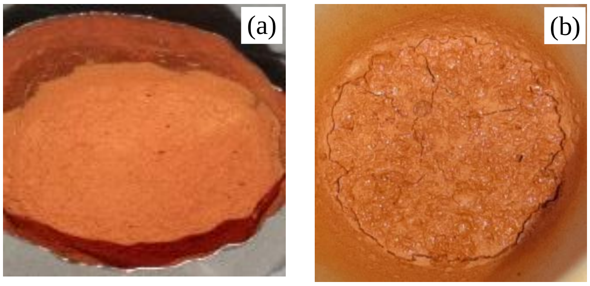

Fig 4. Uranium trioxide with (NH_4^+/U) ratio: (a) between 2 and 3, (b) less than or equal 1.5.

For NH_4^+/U molar ratios between 2 and 3, the liquids evaporate immediately, leaving behind a solid double nitrate salt, which decomposes into a fine powder without melting. Nevertheless, when the NH_4^+/U ratio less than 1.5, the evaporation of the solution leads to the formation of the hexahydrate uranyl salt which has a Melting point much lower than its decomposition temperature, so that a syrupy molten salt is formed during heating [9]. When this molten salt reaches its decomposition temperature, the water vapor and the NO_x gases are released. This leads to splashes and the formation of foam [10,11], and the uranium can be distributed throughout the whole of the chemical reactor.

The evolution of the specific surface area of the various UO_3 powders produced, as a function of the amount of ammonium nitrate (NH_4^+/U molar ratio) is presented in Figure 5. As can be seen, the specific surface increases and then decreases as a function of the NH_4^+/U ratio. In fact, the surface area passes from 1.32 m^2/g for NH_4^+/U equal to 1.5 to the maximum value of 8.71 m^2/g for NH_4^+/U equal to 2.2, then decreases up to 3.68 m^2/g for NH_4^+/U equal to 2.5 to finally stabilize in the range of the NH_4^+/U ratio between 2.5 and 3.0 m^2/g.

According to the literature, there is a correlation between the specific surface and the reactivity of UO_3, this increases when the specific surface increases [10]. In addition, the uranium trioxide prepared by the direct thermal denitration process (NH_4^+/U=0) has low specific surfaces (0.2–1.8 m^2/g), whereas that prepared by the MDD process has higher specific surfaces (5 – 15 m^2/g) [10]. According to the results of figure 4, the specific surface of the UO_3 prepared with the NH_4^+/U ratio equal to 2.2 equal to 8.71 m^2/g is included in the target range 5 to 15 m^2/g, therefore, we can conclude that the addition of ammonium nitrate to the uranyl nitrate solution makes it possible to improve the reactivity of the UO_3.

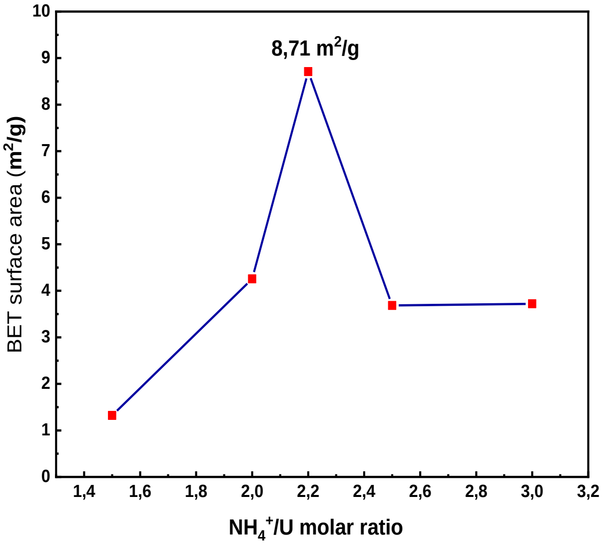

Fig 5. Effect of the NH_4^+/U molar ratio on the specific surface area of UO_3.

3.2 . *Thermogravimetric analysis*

Thermogravimetric analysis was used to determine the steps of the dehydration and thermal decomposition of double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ in nitrogen atmosphere. The sample was heated from ambient to 700 °C at a heating rate of 5 °C/min, using a sample mass of 34.6 mg (figure 6).

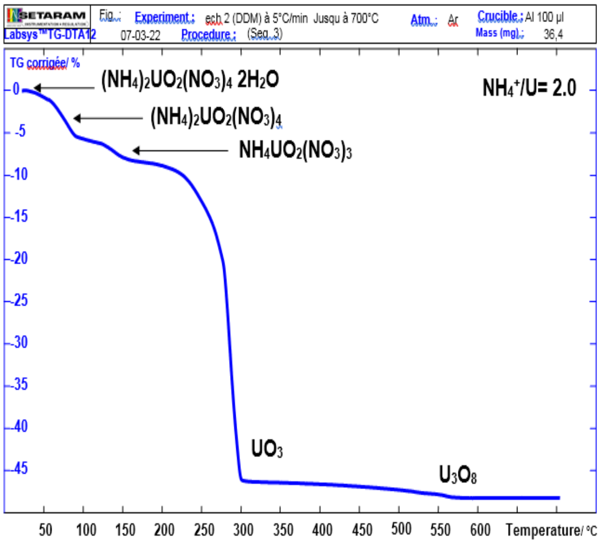

Fig 6. TG curve for the double Salt dihydrate $(NH_4)_2UO_2(NO_3)_4.2H_2O$ in N_2 atmosphere at a heating rate of 5°C/min, with NH_4^+/U molar ratio equal 2.0.

As can be seen, Figure 6 shows four weight loss steps, the first of about 1.65 % (w/w) was due to the dehydration of the double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ at about 50 ° C to form the anhydrous double salt, and the other step starts at about 160°C of 2,23% (w/w) corresponds to the decomposition of the anhydrous tetranitrate salt $(NH_4)_2UO_2(NO_3)_4$ to form a trinitrate salt, with the loss of one mole of ammonium nitrate (NH_4NO_3). In the third step, amorphous uranium trioxide (UO_3) forms after complete decomposition of the trinitrate salt at around 275°C, with weight loss of about 32.36% (w/w), generating volatile compounds, such as N_2O_5, NO_2 and H_2O. In the fourth step, mass loss of 0.47 % (w/w) was observed at about 570 °C, which was attributed to decomposition of UO_3 to U_3O_8.

3.3 . Differential thermal analysis

Figure 7 shows the DTA results from the thermal decomposition of $(NH_4)_2UO_2(NO_3)_4.2H_2O$ in a nitrogen atmosphere. As can be seen, the endothermic reaction began around 50 °C with the dehydration of the double salt leading to an anhydrous double salt:

$$(NH_4)_2UO_2(NO_3)_4.2H_2O \xrightarrow{50°C} (NH_4)_2UO_2(NO_3)_4 + 2H_2O \qquad (2)$$

Endothermic peak between 80 and 100°C, which appeared to be a phase change of ammonium nitrate (NH_4NO_3), is caused by the presence of low proportion of impurities. An endothermic peak as a result of the first decomposition of the anhydrous tetranitrate salt to a trinitrate salt without melting at about 160°C., with the loss of one mole of ammonium nitrate in the form of N_2O and H_2O:

$$(NH_4)_2UO_2(NO_3)_4 \xrightarrow{160°C} NH_4UO_2(NO_3)_3 + N_2O + 2H_2O \qquad (3)$$

A second endothermic peak that was due to the conversion of the salt $NH_4UO_2(NO_3)_3$ to amorphous UO_3 after complete denitration at around 275°C:

$$NH_4UO_2(NO_3)_3 \xrightarrow{275°C} UO_3 + N_2O_5 + N_2O + 2H_2O \quad (4)$$

After the second endothermic peak, an exothermic reaction took place at around 450 C, resulting in the formation of a crystalline form of UO_3 [13]. Finally, an endothermic peak at 570°C, which corresponds to the transformation of UO_3 into stable U_3O_8, with the departure of an oxygen molecule:

$$3UO_3 \xrightarrow{275°C} U_3O_8 + 1/2\,O_2 \qquad (5)$$

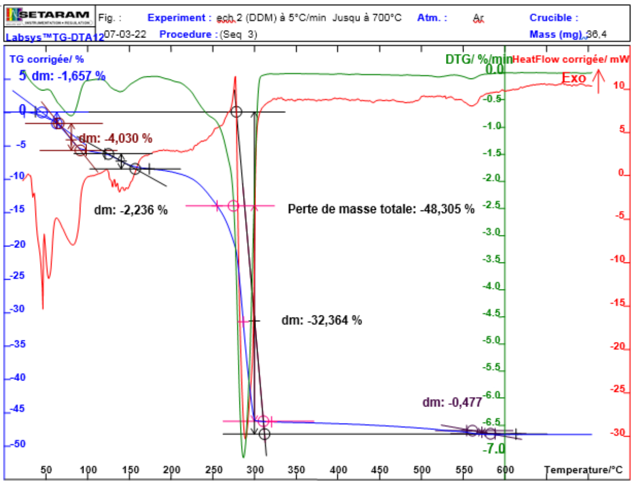

Fig 7. DTA thermograms in N_2 atmosphere at a heating rate of 5°C/min.

3.4 . Thermal decomposition of UO_3

The calcination of the UO_3 powder, at 650 °C for one and two hours, allowed to elaborate oxides whose identification, by UV-visible spectrophotometry gave spectra presented in the figures 8 and 9. It can be seen that U(IV) has maxima at 663 nm. The data associated with the absorption peaks of uranium as well as the calculated O/U ratios are listed in table 2. As can be seen, the O/U ratio decreases with the increase in the calcination. The O/U ratio of the uranium oxide prepared after one hour of calcination, at 650°C is equal to 2.65. This value is close to the theoretical value of U_3O_8 which is 2.67±0.01 [14]. The projection of this value (2.65) on the phase diagram (Fig. 10) shows that it is included in the range of the O/U ratio (2.6-2.66), which suggests that the oxide produced under these conditions is β-U_3O_8 [15]. These results are in agreement with previous studies which have shown that, the UO_3 amorphous form, begin to decompose in air at 400-500°C and can be fully converted to U_3O_8 at about 650°C, which is the stable form [16]. This confirms that a calcination time of one hour and a temperature of 650°C are sufficient to completely transform the UO_3 oxide into a stable β-U_3O_8 oxide.

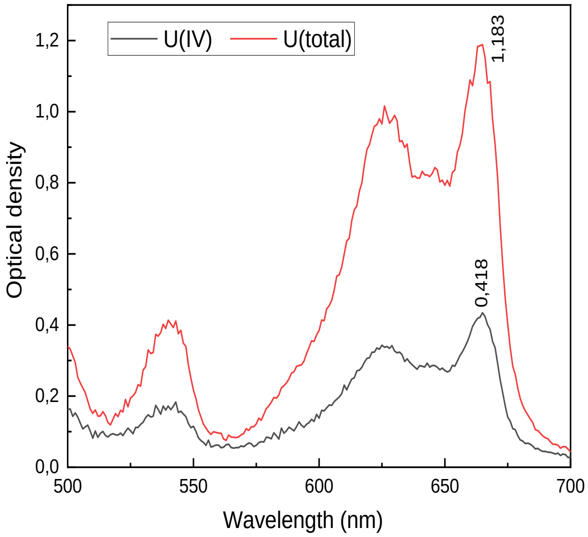

Fig 8. Absorption spectrum of U(total) and U(IV) in a H_3PO_4 solution, obtained after heating of UO_3 for 1 hour at 650 °C.

Table 2. Heating conditions for the preparation of U_3O_8 from UO_3 and O/U ratio of U_3O_8 phase.

Heating temperature (°C)	Calcination Time (h)	Absorbance at 663 nm	O/U ratio
650 °C	01	AU(IV) = 0.418 AU(total) = 1.183	2.65
	02	AU(IV) = 0.492 AU(total) = 1.298	2.62

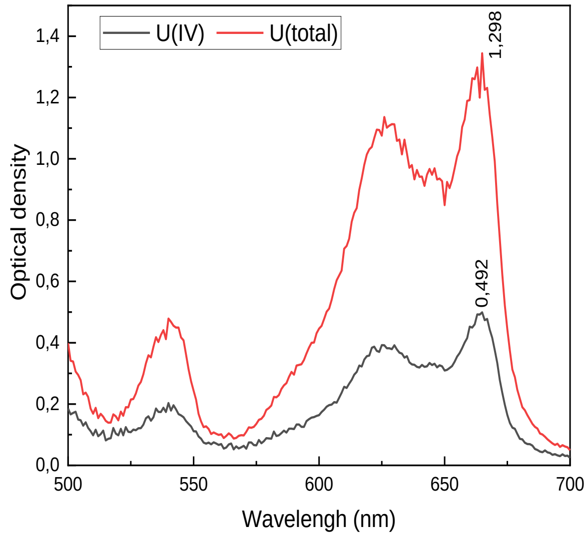

Fig 9. Absorption spectrum of U(total) and U(IV) in a H_3PO_4 solution, obtained after heating of UO_3 for 2 hours at 650 °C.

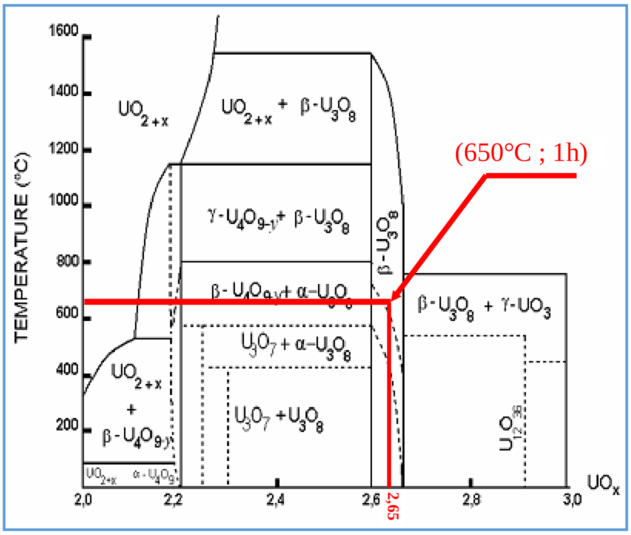

Fig 10. Phase diagram of the Uranium-Oxygen system.

4. Conclusion

The objective of this work is to study the thermal decomposition of double salt $(NH_4)_2UO_2(NO_3)_4.2H_2O$ in air und nitrogen atmosphere by Modified Direct Denitration (MDD) process to a triuranium octoxide powder, in a furnace and by thermogravimetry. The modified direct denitration process is an easy process to set up and which does not require a lot of resources. The TG/ATD analysis of the double salt revealed four mass losses associated with endothermic peaks, due to the formation of phases which are: $(NH_4)_2UO_2(NO_3)_4$ at about 50°C, $NH_4UO_2(NO_3)_3$ at about 160°C, UO_3 amorphous form at 275°C. and U_3O_8 at 570°C. The MDD process allow to produce a UO_3 powder, massive but friable, which has a specific surface area in the target range (5 – 12 m^2/g). The identification of the uranium oxides by the O/U ratio showed that calcination time of one hour and a temperature of 650°C are sufficient to completely transform the UO_3 oxide into a stable β-U_3O_8.

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Conflict of Interest

The authors declare no conflicts of interest regarding this article

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