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Microwave synthesis of solid solutions of urania and thoria – a comparative study

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Abstract

Recently a new route for the production of thoria powder that yields pellets of high density had been communicated. In continuation of this study, the method as applied to the preparation of (U, Th)O_2 powders with various compositions is reported here. The powders were characterised for crystallite size by using XRD and transmission electron microscopy and BET surface area. As observed in the case of thoria, the powders obtained in this study were found to be nanocrystalline. The sinterability of the powder was determined by measuring the density of the sintered pellets prepared from these powders. The sintering was carried out at 1573 K in argon atmosphere. The feasibility of calcining and sintering of the solid solutions by using microwave heating was also studied. © 1998 Elsevier Science B.V.

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1. Introduction

Urania and thoria have calcium fluoride type crystal structure and their lattice parameters are nearly the same [1]. These two oxides form a series of solid solutions throughout the composition range [2]. Solid solutions of uranium and thorium oxide are being developed as fuel for the thermal breeder reactors and high temperature gas cooled reactors. Due to its significance in the nuclear industry, this system has been extensively studied. Methods ranging from direct mixing of the two oxides by conventional powder metallurgy route to sol–gel techniques have been reported for the preparation of (U, Th)O_2 solid solutions [3–9].

Mohan and Moorthy [3] have studied the preparation and sintering behavior of urania–thoria solid solutions in detail. They have prepared the solid solutions by mechanically mixing the two oxides and sintering them at various temperatures ranging from 1523 to 1823 K. They concluded that the formation of solid solutions occurred only on heating the mixtures above 1673 K and that also only when the two oxides were ‘active’ powders; otherwise still higher temperatures were required for the formation of the solid solutions. Matthews and Davies [4] have reported that solid solutions from individual oxides can be accomplished only at 1973 K.

Coprecipitation of thorium and uranium as hydroxides or oxalates and subsequent heating under reducing conditions had been accepted as standard methods for the preparation of homogeneous solid solutions and have been used for preparing homogeneous urania–thoria solid solutions [5,6]. White et al. [5] have studied a coprecipitation method employing oxalic acid as precipitating agent to produce $(U_{0.25}Th_{0.75})O_2$. They have reported the formation of solid solutions on calcining the oxalate precipitate of thorium and uranium (U^{4+}) in air and in He–6% H_2. However, they found that the slow removal of CO and CO_2 evolved due to the decomposition of the oxalate precipitate in a reducing atmosphere could cause reducing conditions in the powder and result in the retention of an unacceptable amount of carbon (5550 ppm). This carbon may interfere with the sintering of the solid solutions to

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high densities. Moreover, the sintering temperature used in the study was 1923 K. Pope and Radford [6] have reported a coprecipitation method employing ammonium hydroxide as the precipitating agent. They also have used temperatures as high as 1923 K to sinter the mixed oxide. A limitation of the coprecipitation method perhaps may be loss of uranium and thorium in the form of dissolved oxalates or hydroxides at the washing stage. The amount of waste generated adds to the limitation.

Yamagishi and Takahashi [7] have recently reported a sol–gel method of preparation of thoria–urania pellets that were sintered at 1573 K in air and subsequently reduced in argon atmosphere to the stoichiometric dioxide. The densities of these pellets were reported to be more than 99% of the theoretical density. However, the integrity of the pellets containing more than 30 mol% urania were found to be not good on reduction to the dioxide. In a later work, pellets with good integrity had been prepared by changing the sintering atmosphere from air to $Ar + 4\%\ H_2$ [8].

The use of microwaves in ceramic processing has been in vogue for sometime [9–16]. It was observed that the microwave heating can lower the processing temperatures by several hundred degrees and shorten the processing time by several hours. Microwave heating not only increases the heating efficiency by concentrating the heating process within the material rather than in the furnace in which it is placed but also has basic consequences such as more efficient atomic diffusion within the material. Microwaves also overcome the problems associated with non-conduction of heat to areas containing unreacted/unaffected material by transferring energy homogeneously and efficiently on a molecular scale throughout the bulk. This ensures uniform heating throughout the body.

Palmer et al. [15] have used a microwave denitration technique to produce thoria–urania solid solutions containing 3 mol% urania. Since details of chemical characterisation of the denitrated product were not given and the product had been calcined at different temperatures it is difficult to assess the feasibility of the technique to large scale production of the urania–thoria solid solutions containing varying amounts of urania and thoria.

Koizumi et al. [16] have successfully used microwaves to produce urania and urania–plutonia solid solutions. They used the direct denitration technique to produce the oxides. However, they had to use additional steps such as reduction and milling to produce ceramic grade oxide powders.

In a recent study [17] a novel method of synthesis of thoria that yielded high density pellets has been reported. The same method was used in this study for the preparation of urania–thoria solid solutions of various compositions. This method involves the denitration of the mixture of the nitrates of uranium (U^{6+}) and thorium in the presence of polyvinyl alcohol (PVA) using a microwave oven. Thoria does not interact with microwaves, whereas urania does interact [18]. An attempt was made to carry out calcination of the denitrated powder and sintering of the pellets using microwaves to study the feasibility of these processes.

The as-denitrated product was found to contain some carbonaceous residue due to the partial decomposition of PVA. In order to remove the carbonaceous material the as-prepared products had to be heated in air. This resulted in the oxidation of samples containing higher urania content. The limit of oxygen solubility in the solid solutions of urania–thoria in bulk has been studied in detail by Cohen and Berman [2]. The powders obtained in our experiments are nanocrystalline. Some of the properties such as solute solubility and specific heat are affected due to nanocrystallinity [19]. Hence, the extent of oxidation of the calcined samples of the $(U, Th)O_2$ solid solutions was studied by measuring the weight loss during the reduction of the calcined powders under $Ar + 5\%\ H_2$ atmosphere using thermogravimetry and X-ray diffraction technique.

2. Experimental

2.1. Chemicals

The polyvinyl alcohol (PVA) of average molecular weight ≈ 77000 was obtained from M/s Loba Chimie Pvt. Ltd., India. Nuclear grade uranium dioxide was obtained from the Nuclear Fuel Complex, India and the thorium nitrate was from M/s Indian Rare Earths, India.

2.2. Experimental procedure

2.2.1. Preparation of urania–thoria solid solutions

Required amounts of aqueous nitrate solutions of uranium (U^{6+}) and thorium corresponding to $U/(U + Th) = 0.15$, 0.50, 0.65 and 0.80 and the aqueous solution of PVA were mixed together. The mixture was then heated in a microwave oven (2450 MHz with variable output from 140 to 700 W) till the whole mixture was completely charred. The as-prepared product was calcined in air at 1073 K for 4 h.

One lot of the solid solutions with $U/(U + Th) = 0.80$ was directly denitrated without the addition of PVA in the microwave oven. The product of direct denitration was also calcined in air at 1073 K for 4 h. For the purpose of comparison with respect to sinterability, one lot of the solid solution with $U/(U + Th) = 0.50$ was prepared by the conventional coprecipitation route using ammonium hydroxide as the precipitant. The precipitate thus obtained was filtered, washed with dilute ammonia (aqueous solution), subsequently with distilled water and then with alcohol, dried under an IR lamp and heated at 1073 K in air.

2.2.2. Calcination using microwave

A few lots of the as-prepared product with high urania content ($U/(U + Th) \geq 0.50$) were transferred into a silica crucible and heated in the same microwave oven for a few minutes till the carbonaceous material was removed. This could be observed as appearance and disappearance of a flame. Heating was stopped soon after the disappearance of the flame.

2.2.3. Sintering studies

The sinterability of all the calcined powders was determined by pressing the powders at 200 MPa into 10 mm diameter pellets in a single action press and sintering them at 1573 K for 4 h in a stream of flowing argon (flow rate 1.4×10^{-6} m^3 s^{-1}) in a molybdenum wire wound resistance furnace. The density of the sintered pellets was measured by liquid immersion technique by employing dibutyl phthalate as the immersion liquid. The densities reported are an average density of 10 pellets. A few lots of pellets with $U/(U+Th) \geq 0.50$ were sintered in the microwave oven under flowing high purity nitrogen gas.

2.2.4. Thermal studies

The extent of oxidation of the solid solutions was studied by measuring the O/M (oxygen/metal) ratio of the calcined powders. This was carried out by heating the air calcined samples at the rate of 5 K/min in flowing high purity argon + 5% hydrogen mixture. The thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a thermal analyser (model: STA 1500 supplied by M/s P L Thermal Sciences, USA).

2.2.5. Characterisation of the samples

Elemental analyses of uranium and thorium were carried out to determine the composition of the mixed oxide. Thorium and uranium were determined by using a complexometric titration. About 200 mg of the oxides were dissolved in concentrated nitric acid with a few drops of dilute HF and heating under IR lamp till dryness. The residue was quantitatively transferred into a standard flask using double distilled water. Thorium in 1 ml or 0.5 ml aliquots was titrated against diethylenetriaminepentaacetic acid (DTPA) using xylenol orange as the indicator [20]. Then to the same aliquot sufficient acetic acid buffer was added to adjust the pH to be between 3 and 4. Then uranium was titrated against pyridine 2,6-dicarboxylic acid (PDCA) using arsenazo-I as indicator [21]. The carbon in the as-prepared product and calcined product was determined by heating the sample in an induction heater in oxygen atmosphere and measuring the carbon dioxide thus generated using an IR detector.

X-ray powder patterns of the as-prepared, calcined and sintered samples were obtained by using a Siemens D 500 X-ray diffractometer employing Cu Kα radiation. The average crystallite size was measured by line broadening technique employing the Scherrer formula [22] using the profiles of the (220) peak. Standard silicon was used for estimation of the instrumental broadening.

All the calcined samples were characterised for BET surface area by using the Nelsen and Eggertsen technique [23]. For this purpose a surface area analyser (model: Quantasorb Jr. supplied by M/s Quantachrome, USA) was used.

As-prepared and conventionally calcined powders of the solid solutions with $U/(U+Th) = 0.15$ and 0.50 and one sample each of microwave calcined and conventionally calcined powder with $U/(U+Th) = 0.80$ were characterised for microstructure and morphological characteristics using a Philips EM400 transmission electron microscope operating at 120 kV. Diffraction contrast techniques including bright field imaging and selected area diffraction (SAD) studies were employed to determine the powder particle size, crystallite size and morphology. Specimens were prepared for microscopy as described earlier [17].

Scanning electron microscopy was carried out on some representative samples of sintered pellets with $U/(U+Th) = 0.15$, 0.50 (sintered in a conventional furnace), 0.65 (microwave sintered) and 0.80 (sintered in a conventional furnace) using JEOL JSM-840 unit.

3. Results and discussion

3.1. Denitration

Denitration of the mixtures of uranium and thorium nitrates in the presence of PVA in air leads to the formation of (U, Th) oxide solid solutions, irrespective of the uranium content. However, the denitration is observed to be less violent with the increase in uranium content. In all the cases the as-prepared product is gray in colour, and highly porous as observed in the case of the denitration of thorium nitrate in the presence of PVA [17]. In order to study the possible mechanism, solid PVA was added to the aqueous solution of nitric acid. Immediately, even before heating, brown fumes were seen as a result of violent reaction between PVA and nitric acid. Eventually, there was no trace of solid PVA. Experiments were carried out with aqueous solutions of PVA mixed with (i) HCl, (ii) NaCl, (iii) $NaNO_3$ and (iv) $NaNO_2$. All the mixtures were heated under the same conditions in the microwave oven. With HCl, complete charring was seen. With NaCl no change was observed. With $NaNO_3$ an explosive reaction with a flame was observed. In the case of $NaNO_2$ there was partial charring. This indicates that for oxidation of PVA, both H^+ and NO_3^- play a role. In the actual experiment, the vigorous reaction observed is due to the reaction of PVA with nitric acid. Since the amount of nitric acid available is negligible in the initial stage of the reaction, the reaction is less vigorous. After partial dehydration of the aqueous solutions, the nitrates decompose to give nitrogen dioxide and oxygen [24,25] as

$$UO_2(NO_3)_2 \cdot nH_2O \rightarrow UO_3 + 1.86NO_2 + 0.14NO + 0.57O_2 + nH_2O. \quad (1)$$

$$Th(NO_3)_4 \cdot 5H_2O \rightarrow ThO_2 + 4NO_2 + 2O_2 + 5H_2O. \quad (2)$$

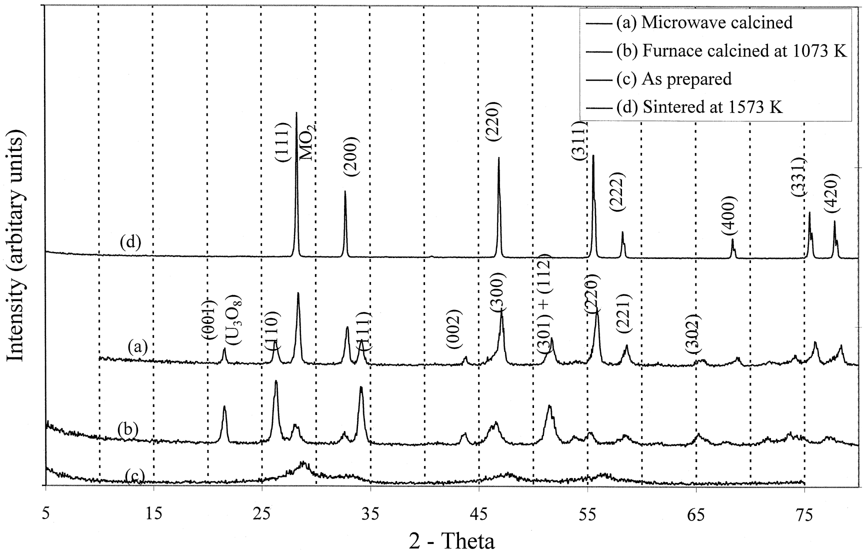

Fig. 1. XRD pattern of the as-prepared sample, the powder calcined at 1073 K, calcined using microwave and sintered sample of $(U_{0.80}Th0_{0.20})O_2$. The peaks corresponding only to U_3O_8 are marked in pattern (a) for clarity, eventhough MO_2 is also present. Patterns (a) and (b) are similar.

The NO_2 thus formed dissolves in the excess water to form nitric acid which starts oxidising the PVA. The oxidation of the PVA is seen from the change in colour of the initial solution from lemon yellow to orange red and finally to dark brown. However, the nitric acid available is not sufficient to complete the oxidation of PVA. The reaction is violent because of the exothermicity of the denitration [24] and oxidation of the PVA. The product of denitration is porous because of the evolution of excessive gaseous material. Thus the PVA provides a surface for the denitration while preventing aggregation and sintering of particles, thereby helping the formation and stabilisation of the nanocrystallinity of the powders. Since PVA is only partially oxidised in the process, thus leaving behind a carbonaceous residue, the solid solution formed does not undergo oxidation to higher oxides even though the deni-

Table 1
Urania–thoria solid solution compositions prepared and the sintered densities obtained

Composition	Calcination by (Cf/Mw)[a]	BET surface area (m^2 g^{-1})	Sintering method (Cf/Mw)[a]	Sintered density (Mg m^{-3})	Lattice parameter (nm)
$(U_{0.15}Th_{0.85})O_2$	Cf 1073 K/4 h	8.86	Cf 1573 K/4 h/argon	9.3 ± 0.13	0.5569 ± 0.0001
$(U_{0.15}Th_{0.85})O_2$	Mw	14.79			
$(U_{0.50}Th_{0.50})O_2$	Cf 1073 K/4 h	4.82	Mw	8.9 ± 0.3	0.55144 ± 0.00005
$(U_{0.50}Th_{0.50})O_2$	Mw	1.8	Mw	9.6 ± 0.6	
$(U_{0.50}Th_{0.50})O_2$	Cf 1073 K/4 h	2.14	Cf 1573 K/4 h/argon	9.5 ± 0.2	
$(U_{0.50}Th_{0.50})O_2$	Mw	1.8	Cf 1573 K/4 h/argon	< 7.0	
$(U_{0.65}Th_{0.35})O_2$	Cf 1073 K/4 h	3.74	Cf 1573 K/4 h/argon	9.6 ± 0.2	0.5512 ± 0.0001
$(U_{0.65}Th_{0.35})O_2$	Cf 1073 K/4 h	3.74	Mw	8.98 ± 0.24	
$(U_{0.65}Th_{0.35})O_2$	Mw	0.83	Cf 1573 K/4 h/argon	9.18 ± 0.2	
$(U_{0.65}Th_{0.35})O_2$	Mw	0.83	Mw	8.82 ± 0.38	
$(U_{0.80}Th_{0.20})O_2$	Cf 1073 K/4 h	2.23	Cf 1573 K/4 h/argon	9.98 ± 0.35	0.54887 ± 0.00007
$(U_{0.80}Th_{0.20})O_2$	Mw	2.03	Mw	7.2-9.08	
$(U_{0.80}Th_{0.20})O_2$	Mw	1.12	Cf 1573 K/4 h/argon	9.74 ± 0.09	
$(U_{0.80}Th_{0.20})O_2$ dir. denitrated	Cf 1073 K/4 h	4.62	Cf 1573 K/4 h/argon	9.71 ± 0.25	
$(U_{0.50}Th_{0.50})O_2$ coprecipitation (ADU + Th hydroxide)	Cf 1073 K/4 h	8.79	Cf 1573 K/4 h/argon	8.74 ± 0.2	

[a] Cf = conventional furnace; Mw = microwave oven.

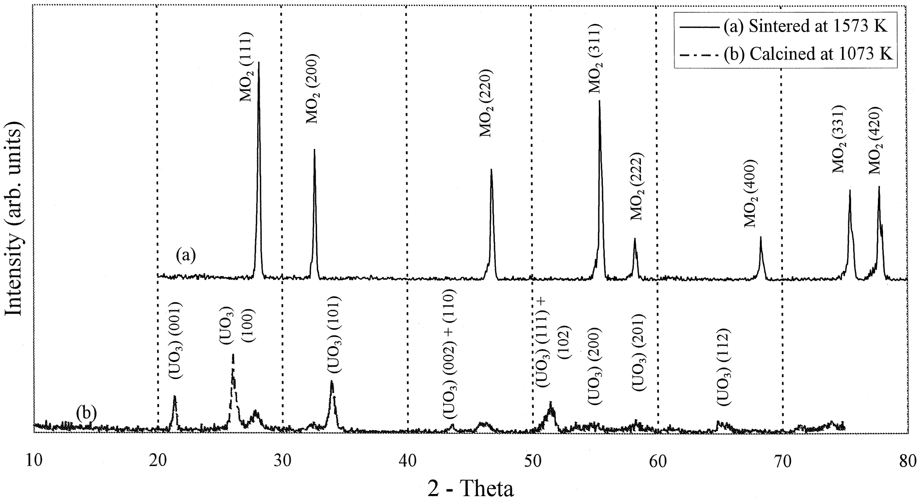

Fig. 2. XRD pattern of the $(U_{0.80}Th_{0.20})O_2$ prepared by direct denitration: calcined and sintered. For clarity peaks corresponding only to UO_3 are marked in pattern (b).

tration is carried out in air. However, Koizumi et al. [16] reported the formation of UO_3 on direct denitration of the aqueous solution of uranyl nitrate in the microwave oven.

The product of direct denitration in this study was reddish yellow in colour. Even though the U/(U + Th) ratio was 0.80, the product did not couple with the microwaves, thereby indicating that the product might be containing UO_3 (Haas [18] reported that among the oxides of uranium, uranium trioxide alone does not interact with the microwaves).

3.2. XRD studies

The as-prepared product obtained from the microwave oven is found to be a (U, Th)O_2 solid solution with cubic structure irrespective of the uranium content. This product on calcination, whether it be in a conventional furnace or microwave oven, yields an oxidised product MO_{2+x} (M = U, Th). The presence of MO_{2+x} is seen from the orange brown colour of the calcined product in the case where U/(U + Th) = 0.15, which turns into bluish green on sintering at 1573 K. The orange brown colour may be due to the presence of U^{6+} [5]. The XRD patterns of the calcined product of the solid solutions with U/(U + Th) = 0.15 and 0.50 are similar to the patterns obtained for the as-prepared product. The expected non-stoichiometry (x) on oxidation at temperatures ≤ 1473 K is reported to be between 0 and 0.25 for U/(U + Th) ≤ 0.50 [1,2]. In cases where the uranium/total metal ratio is > 0.50, the formation of a

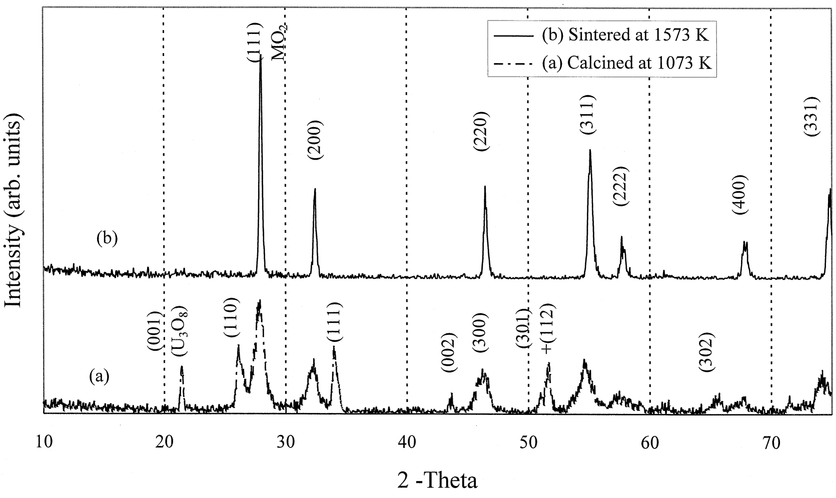

Fig. 3. XRD pattern of the $(U_{0.50}Th_{0.50})O_2$ prepared by coprecipitation: calcined and sintered. Only the peaks corresponding to U_3O_8 have been marked in pattern (a) for clarity.

second phase (orthorhombic U_3O_8) apart from the cubic phase is reported on oxidation of (U, Th)O_2 [1,2]. The XRD patterns of the as-prepared, calcined (by conventional furnace and microwave oven) and sintered samples with $U/(U+Th)=0.80$ are given in Fig. 1. It can be seen from the figure that on calcination (by both conventional and micrwave oven) of the as-prepared sample a second phase is observed and is found to be hexagonal α-U_3O_8 and is found in high urania ($U/(U+Th)>0.50$) containing solid solutions. This second phase is found to disappear on heating at 1573 K under flowing argon (perhaps due to thermal decomposition of the U_3O_8) as evidenced by XRD patterns of the as-prepared, calcined and sintered solid solutions with $U/(U+Th)=0.80$ shown in Fig. 1. According to Paul and Keller [26] thoria is not soluble in U_3O_8 which means that the precipitation of U_3O_8 must result in the depletion of uranium in the solid solution. The XRD patterns in Fig. 1 indicate that the precipitation of the second phase indeed results in uranium depletion in the solid solution. This is seen as a slight shift in the peak positions of the calcined sample towards the high thorium side (lower 2θ values) with respect to the sintered and the as-prepared samples. Typical values of the lattice parameters calculated from the XRD patterns of sintered samples of the differant compositions are listed in Table 1.

The calcination of the directly denitrated product results in α-UO_3 in addition to the solid solution MO_{2+x}. This is shown in the XRD pattern of the calcined product in Fig. 2. On the other hand, the calcined product of the coprecipitated ammonium diuranate and thorium hydroxide seems to be as indicated by the XRD pattern given in Fig. 3 namely the presence of α-U_3O_8 in addition to MO_{2+x}.

The crystallite size of all the as-prepared powders was ≈ 3 nm. The crystallite size of the calcined powders varied from 8 to 10 nm depending on the urania content. The microwave calcined solid solutions had a crystallite size of ≈ 25 nm. The crystallite size of the conventionally sintered product was found to be about 25 to 30 nm. The conventionally calcined product of coprecipitation had a crystallite size of 8.2 nm.

3.3. CTEM studies

The results of the analysis using the CTEM are presented in Figs. 4–6. The as-prepared solid solution with $U/(U+Th)=0.15$ is composed of particles of 0.2 to 0.4 μm size, showing a mottled microstructure. At higher magnification (Fig. 4(a)) these were resolved and measured to be in the range 8–13 nm. For the calcined sample the measured particle size was about 0.75 μm. Selected area diffraction (SAD) gave ring patterns (Fig. 4(b)) corresponding to the cubic structure. This indicates that the particles are composed of finer crystallites. The nanocrystalline grain size was found to be 6 nm. Fig. 5 gives the bright field image for the as-prepared and conventionally calcined solid solution powder with $U/(U+Th)=0.50$. Fig. 5(a) shows a nanocrystalline agglomeration including filamentary structures corresponding to residual carbon. The nanocrystallite sizes are larger compared to other samples (21–28 nm). This is supported by the rings in the diffraction patterns (Fig. 5(b)) being spotty. The presence of the filamentary structures also increases the diffused background in the pattern. Nanocrystals in the absence of the filamentary structures show a slightly smaller size of 16 nm. However, the conventional calcination of the above powder resulted in a particle size and crystallite size of 0.2 μm and 4.5 to 6 nm, respectively.

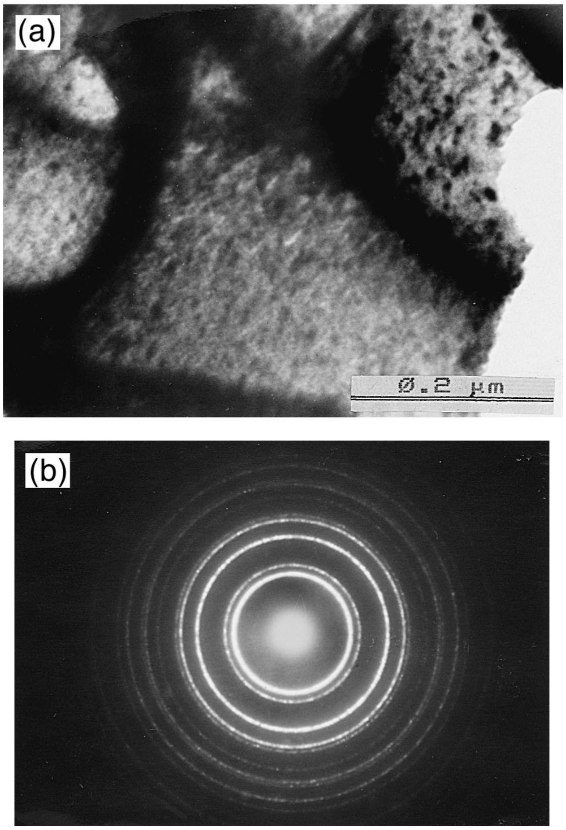

Fig. 4. CTEM of $(U_{0.15}Th_{0.85})O_2$ powder. (a) As-prepared $(U_{0.15}Th_{0.85})O_2$ powder; (b) selected area diffraction pattern of calcined $(U_{0.15}Th_{0.85})O_2$ powder.

Fig. 6(a) and (b) show a comparison of the microwave calcination with the conventional calcination. In Fig. 6(a), the pattern for the microwave calcined solid solution with $U/(U+Th)=0.80$ is given. Here, residual carbon with filamentary structures is seen. The crystallite size is in the 16–23 nm range. The conventionally calcined powder shows a typical particle size of 0.45 μm and an average crystallite size of 8.6 nm. Here again, the rings in the SAD correspond only to the cubic structure and no other phase except the cubic phase is seen. This discrepancy between

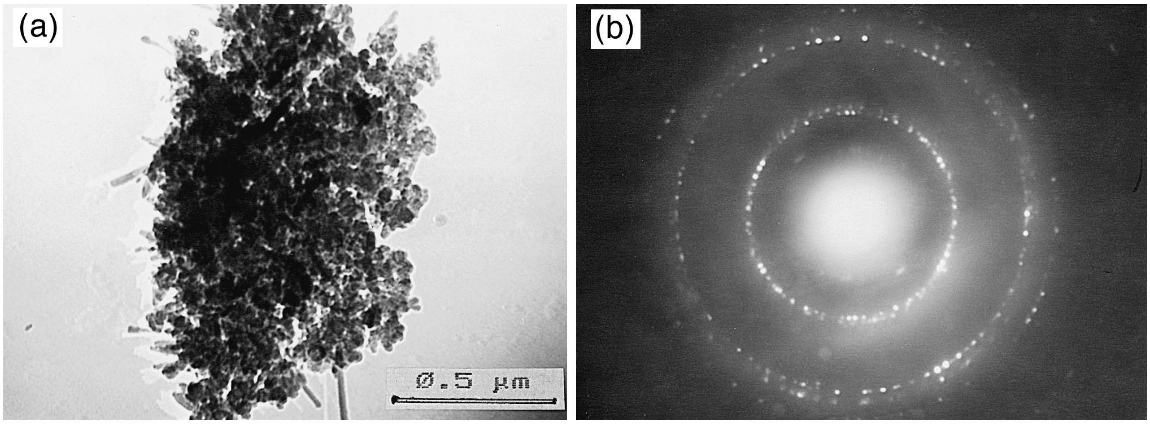

Fig. 5. CTEM of $(U_{0.50}Th_{0.50})O_2$ powder. (a) As-prepared $(U_{0.50}Th_{0.50})O_2$; (b) selected area diffraction pattern of conventionally calcined $(U_{0.50}Th_{0.50})O_2$.

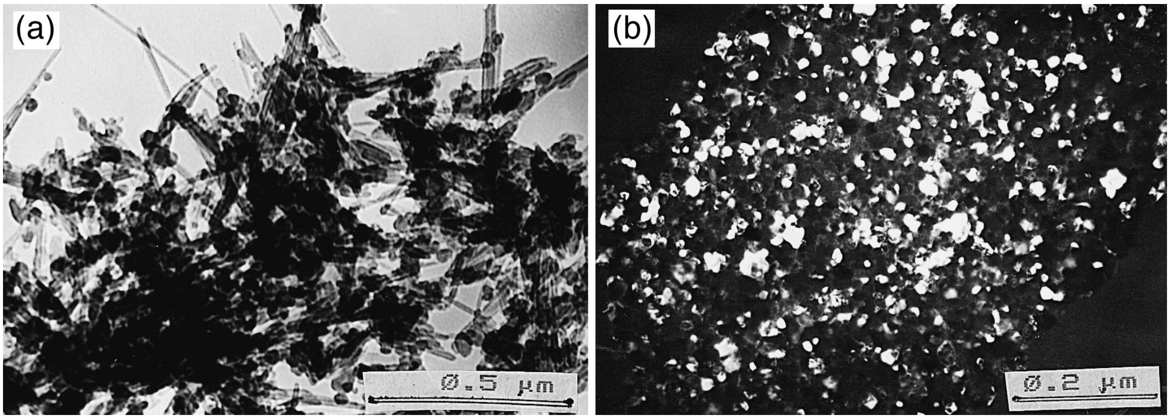

Fig. 6. CTEM of $(U_{0.80}Th_{0.2})O_2$ powder. (a) Microwave calcined $(U_{0.80}Th_{0.20})O_2$; (b) conventional furnace calcined $(U_{0.80}Th_{0.2})O_2$.

the XRD and TEM results is perhaps due to the very small volume fraction of the additional phases such as α-U_3O_8.

3.4. Surface area

The BET surface area of the calcined powders as a function of composition of the solid solution and the method employed for calcination are listed in Table 1. As the $U/(U + Th)$ ratio increases, the surface area of the conventionally calcined powders is found to decrease. The microwave heating to remove the carbonaceous material resulted in low surface area powders as reflected by larger crystallite sizes. This may be due to the effective coupling of urania with microwave resulting in aggregation of the crystallites. $(U, Th)O_2$ solid solutions with $U/(U + Th) = 0.15$ could not be heated using microwave. Hence, a secondary heating using graphite as a coupling agent was employed for the calcination. The BET surface area of this powder was found to be almost twice the area of the powder obtained by calcining in a conventional furnace – perhaps the temperatures reached in the microwave heating may be less than that obtained with the conventional furnace. However, the carbon content also was found to be higher. The carbon contents in the as-prepared and calcined powders are listed in Table 2. It is seen that the microwave heating is equally effective as compared with conventional heating for the removal of carbon. Further, the microwave calcining of solid solutions with $U/(U + Th) > 0.50$ resulted in relatively purer (phase purity) solid

Table 2
Carbon content in the samples prepared

Composition	Carbon content (wt%)		
	as-prepared product	calcined product	
		microwave	conv. furnace
$(U_{0.15}Th_{0.85})O_2$	5.7	0.39	0.11
$(U_{0.50}Th_{0.50})O_2$	2.9	0.08	0.02
$(U_{0.80}Th_{0.20})O_2$	4.3	0.05	0.02

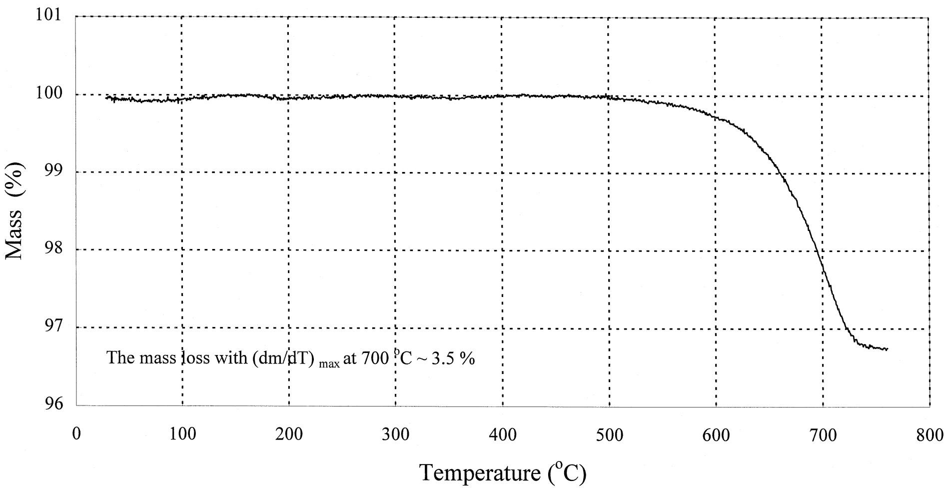

Fig. 7. Thermogram of the calcined $(U_{0.80}Th_{0.20})O_2$.

solution as seen in the XRD pattern of the microwave calcined solid solution with $U/(U+Th) = 0.80$ shown in Fig. 1.

3.5. Thermal studies

The calcined solid solutions with $U/(U+Th) = 0.15$ were orange brown whereas the sintered pellets were bluish green in colour. The thermograms of the as-prepared and sintered solid solutions with $U/(U+Th) = 0.15$ indicated no weight loss, meaning that the as-prepared product and the sintered product essentially are single-phase MO_2. The calcined product of the solid solution with $U/(U+Th) = 0.50$ was dark green whereas the sintered pellets were bluish green. However, solid solutions with $U/(U+Th) > 0.50$ were dark green which on sintering showed no significant change in colour. The thermogram of the calcined thoria–urania with $U/(U+Th) = 0.80$ is shown in Fig. 7. The high urania containing calcined solid solution on reduction in the argon–hydrogen atmosphere gave up to 3.5% weight loss indicating that the O/M of the two-phase mixture changed from 2.67 to 2.00 and this reduction occurs at around 823 K. The DTA plot (Fig. 8) of the reduction of the above solid solution indicated that a phase change is involved during the calcination step as indicated by a strong exotherm peak. The calcined product has been identified as hexagonal α-U_3O_8 in addition to the solid solution by XRD. Cohen and Berman [2] while studying the oxidation behavior of the $(U, Th)O_2$ solid solutions reported the formation of orthorhombic U_3O_8 for $U/(U+Th) > 0.50$, at temperatures ≤ 1473 K. Recently, De Lima and Imakuma [27] have reported the formation of

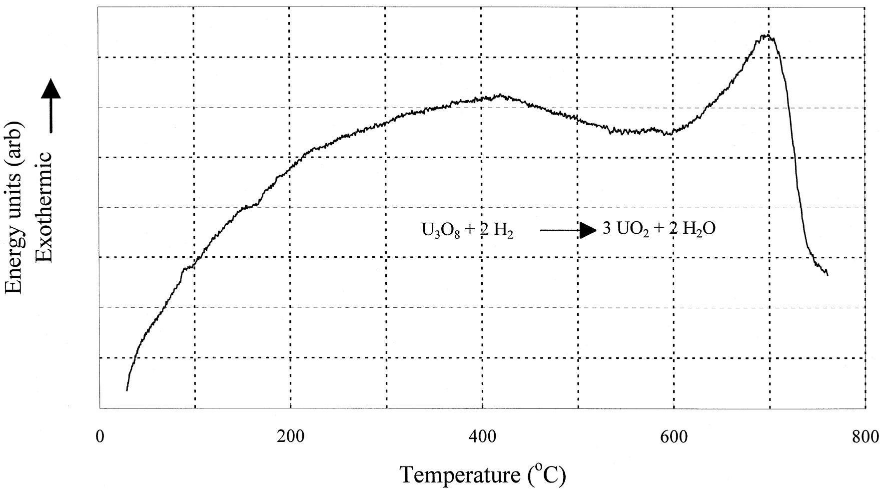

Fig. 8. DTA of the calcined $(U_{0.80}Th_{0.20})O_2$ sample.

a pseudo-hexagonal orthorhombic phase in a similar study. Loopstra [28] suggested that the pseudo-hexagonal U_3O_8 structure is almost similar to the orthorhombic and the transformation from the pseudo-hexagonal orthorhombic to the pure hexagonal phase occurs at about 483 K. In this study the formation of hexagonal α-U_3O_8, a high temperature phase, may perhaps be explained on the basis of the nanocrystallinity of the material.

3.6. Sintering studies

Densities of the sintered pellets are given in Table 1. The low urania containing solid solution did not effectively couple with the microwaves. Hence, sintering of the pellets with $U/(U+Th)=0.15$ could not be carried out employing microwave heating. While high density pellets of other compositions could be prepared consistently using conventional heating, pellets could not be densified to high densities reproducibly in microwave heating perhaps due to practical difficulties in providing sufficient thermal insulation for the pellets during heating. Due to experimental limitations in the control of sintering atmosphere, microwave sintering of the pellets of powders with $U/(U+Th)>0.50$ yielded only lower density pellets containing higher oxide perhaps due to inefficient removal of oxygen during the thermal decomposition of the higher oxide. Even though the calcined product of the powder obtained by coprecipitation was nanocrystalline, the density obtained was only 8.74 ± 0.2 Mg m^{-3} as compared to the density of 9.5 ± 0.2 Mg m^{-3} obtained using the PVA aided denitrated powder.

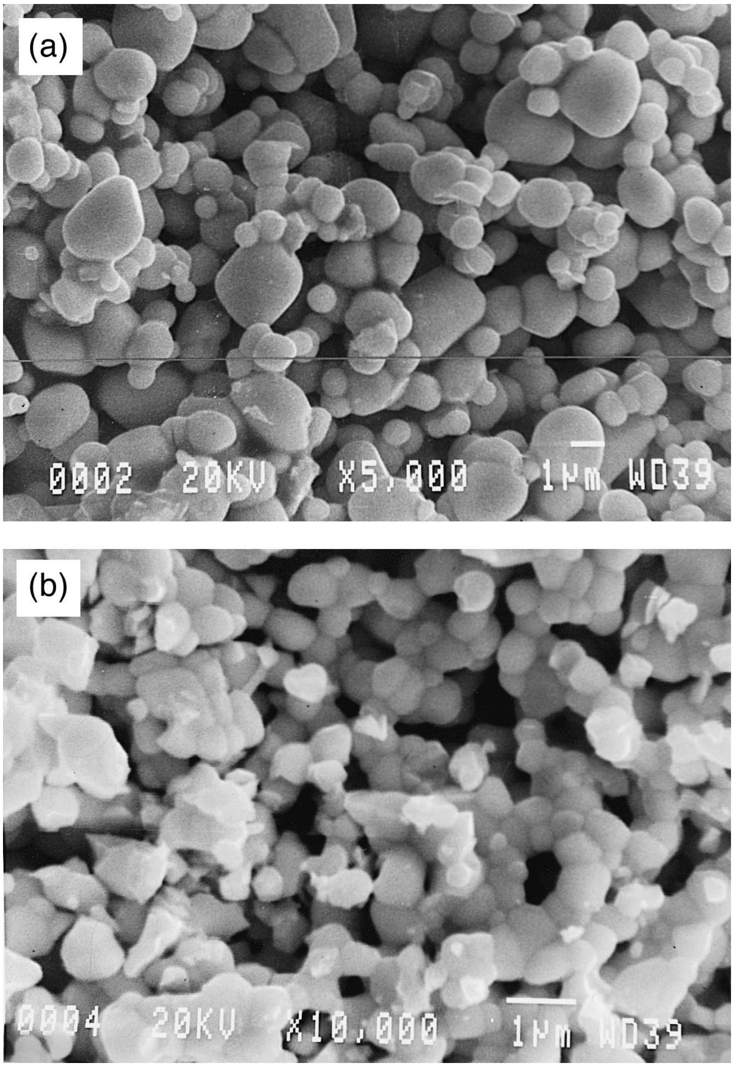

Fig. 9. Scanning electron micrographs of conventionally sintered pellets. (a) $(U_{0.50}Th_{0.50})O_2$ pellet surface showing bimodal distribution of grains; (b) $(U_{0.80}Th_{0.20})O_2$ pellet surface.

SEM micrographs of the pellets with $U/(U+Th)=0.50$ and 0.80 both conventionally sintered are shown in Fig. 9(a) and (b). The micrographs of $U/(U+Th)=0.50$ (Fig. 9(a)) indicates grains of spherical shape with a bimodal distribution in sizes. While the larger grains are approximately 2 μm in diameter the smaller ones are 1 μm in diameter. However, the agglomeration is less pronounced in these samples. The micrograph of $U/(U+Th)=0.80$ pellets (Fig. 9(b)) indicates a more uniform grain size distribution (average size being 0.5 μm). The morphology of the grains is similar to that of the two previous cases.

4. Conclusion

Homogeneous solid solutions containing uranium and thorium oxides with $U/(U+Th)=0.15$, 0.50, 0.65 and 0.80 have been successfully prepared using the PVA aided denitration method in a microwave oven. Excepting the case of $U/(U+Th)=0.15$, microwave calcining of the denitrated powders resulted in powders with lower surface area compared to the conventionally calcined powders. The density obtained with microwave calcined powders that were sintered using a conventional furnace was comparable with that obtained using conventional techniques. However, microwave calcination resulted in relatively phase-pure solid solutions perhaps due to shorter processing time namely 2 min as compared to 4 h at 1073 K. Sinterability studies indicate that the solid solutions may be sintered to high densities at lower temperatures using conventional heating techniques. Microwave sintering of the solid solutions does not always yield high densities. Perhaps a detailed study of the extent of sintering as a function of microwave power might be required to assess the feasibility of the microwave sintering. The solid solutions with $U/(U+Th)\leq 0.50$ exist as a single phase having a cubic structure, while those with $U/(U+Th)>0.50$ lead to a two-phase mixture containing hexagonal α-U_3O_8 and cubic MO_{2+x} on oxidation at temperatures ≥ 1073 K in air. This is true for the solid solutions prepared using the PVA aided denitration.

As in the case of pure thoria prepared by PVA aided denitration, the powder sizes were found to be in the nanocrystalline range agglomerated into larger particles. These larger agglomerates were of 0.5 to 1.0 μm size while the crystallites within were in the nanometer range. Residual carbon with a filamentary morphology with embedded nanocrystallites of the solid solutions were seen in the as-prepared and the microwave calcined powders. Diffraction experiments showed that the phases corresponded to the cubic structure expected of solid solution of (U, Th)O_2. No additional phases were seen even in the samples with $U/(U+Th)>0.50$.

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References

[1] J. Belle, R.M. Berman, Thorium Dioxide: Properties and Nuclear Applications, DOE/NE-0060 (1984).

[2] I. Cohen, R.M. Berman, J. Nucl. Mater. 18 (1966) 77.

[3] A. Mohan, V.K. Moorthy, BARC-568 (1971).

[4] R.B. Matthews, N.C. Davies, PNL-3210 (1979).

[5] G.D. White, L.A. Bray, P.E. Hart, J. Nucl. Mater. 96 (1981) 305.

[6] J.M. Pope, K.C. Radford, J. Nucl. Mater. 52 (1974) 241.

[7] S. Yamagishi, Y. Takahashi, J. Nucl. Mater. 217 (1994) 127.

[8] S. Yamagishi, Y. Takahashi, J. Nucl. Mater. 227 (1995) 144.

[9] B. Riley, in: P.P. Vincezini (Ed.), Ceramics Today — Tomorrow's Ceramics, Elsevier, 1991, p. 1283.

[10] K.J. Rao, P.D. Ramesh, Bull. Mater. Sci. 18 (1995) 447.

[11] L.M. Sheppard, Am. Ceram Soc. Bull. 67 (1988) 1656.

[12] M.A. Janney, C.L. Calhoun, H.D. Kimrey, in: D.E. Clark, F.D. Gac, W.H. Sutton (Eds.), Proc. Symp. on Microwaves: Theory and application in Materials Processing, Am. Ceram. Soc., Cincinnati, OH, Ceram. Trans. 21 (1991) 311.

[13] M.A. Janney, C.L. Calhoun, H.D. Kimrey, J. Am. Ceram. Soc. 75 (1992) 341.

[14] I. Ahmad, G.T. Chandler, D.E. Clark, in: W.H. Sutton, M.H. Brooks, J. Chabinsky (Eds.), Proc. Mater. Res. Soc. Symp on Microwaves in Processing of Materials, Mater. Res. Soc., vol. 124 (1988) 239.

[15] B.J.F. Palmer, L.E. Bahen, A. Celli, Am. Ceram. Soc. Bull. 63 (1984) 1030.

[16] M. Koizumi, K. Ohtsuka, H. Isagawa, H. Akiyama, A. Todokoro, Nucl. Tech. 61 (1983) 55.

[17] V. Chandramouli, S. Anthonysamy, P.R. Vasudeva Rao, R. Divakar, D. Sundararaman, J. Nucl. Mater. 231 (1996) 213.

[18] P.A. Haas, Am. Ceram. Soc. Bull. 58 (1979) 873.

[19] D. Sundararaman, Mater. Sci. Eng. B 32 (1995) 307.

[20] E. Celon, S. Degetto, G. Marangoni, L. Baracco, Talanta 26 (1979) 160.

[21] R. Pribil, V. Vaseley, Talanta 10 (1963) 899.

[22] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York, 1954.

[23] F.M. Nelson, F.T. Eggertsen, Anal. Chem. 30 (1958) 1387.

[24] R.N. Tiwari, D.N. Sinha, Indian Chem. J. 14 (1980) 25.

[25] A.A. Jonke, E.J. Petkus, J.W. Loeding, S. Lawroski, Nucl. Sci. Eng. 2 (1957) 303.

[26] R. Paul, C. Keller, J. Nucl. Mater. 41 (1971) 133.

[27] N.B. de Lima, K. Imakuma, J. Nucl. Mater. 135 (1985) 215.

[28] B. Loopstra, J. Appl. Crystall. 3 (1970) 94.