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Thoria doped with cations of group VB–synthesis and sintering

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Abstract

The cations M^{5+} ($M = V$, Nb and Ta) were doped in thoria through gel-combustion synthesis using citric acid as fuel. Thorium dioxide feed powders thus prepared were cold compacted without binder or lubricant and sintered to a high density ($\geqslant 9.5$ Mg m^{-3}) at relatively low temperatures ($\leqslant 1623$ K). The powders were characterised for the residual carbon, crystallite size, specific surface area, particle size distribution and bulk density. The distribution of the dopant in the thoria matrix was analyzed by electron probe microanalysis. The reactivity of the calcined powders was determined by measuring the density of the sintered compacts prepared from them. For the first time it is demonstrated that apart from niobia, even tantala and vanadia can bring about accelerated sintering in thoria if they are doped through a wet chemical route viz., the gel-combustion procedure. The maximum densities obtained by doping with vanadia (0.02 mol%), niobia (0.50 mol%) and tantala (0.50 mol%) were 9.8 Mg m^{-3} (1573 K), 9.68 Mg m^{-3} (1423 K) and 9.69 Mg m^{-3} (1623 K), respectively. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium dioxide finds extensive applications in the nuclear industry. Pellets of thoria are used in PHWRs and FBRs as blanket material. By virtue of its chemical inertness and high melting point, thorium dioxide is used as an ideal ceramic container for many molten metals and alloys [1]. In all these applications, ceramic bodies with high densities (>96% TD) fabricated out of thoria are used. The conventional methods employed to fabricate high density thoria require very high temperatures (1773–1973 K) [2] and are energy and cost intensive. Hence, there is a need to develop 'advanced methods' for the fabrication of thoria bodies with high density.

Various energy efficient methods, which employ temperatures lower than 2073 K have been developed by different workers [2–18], for the fabrication of thoria ceramics with high density. Pope and Radford [2] described a procedure based on the denitration of thorium nitrate. Recent work carried out in our laboratory [17] shows that sintered pellets with densities as high as 9.6 Mg m^{-3} could be obtained by sintering the thoria powders derived from 'de-agglomerated' thorium oxalate at 1873 K. Gel-combustion synthesis has been employed for preparing nanocrystalline, surface active powders of thoria as well as the solid solutions containing thoria [9–16]. Chandramouli et al. [10] synthesized 'surface-active' thoria powders using a gel-combustion method. These powders could be sintered up to a maximum density of 9.6 Mg m^{-3} at temperatures as low as 1573 K. Purohit et al. [16] synthesised nanocrystalline thoria by a combustion procedure in which glycine was used as the fuel. These powders could be sintered to a maximum density of 9.7 Mg m^{-3} at 1573 K.

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It is well known that the addition of aliovalent cations accelerates the sintering of thoria [6–8,18]. Balakrishna et al. [6] demonstrated that thoria could be sintered to densities as high as 9.76 $\mathrm{Mg\,m^{-3}}$ at 1423 K by doping with 0.25 mol% Nb_2O_5. In another study, Balakrishna et al. [7] demonstrated that, the effect of addition of higher valence additives, viz., niobia, vanadia and tantala on the densification of thoria is positive. However, these authors also observed that the very high degree of densification found in thoria doped with niobia was not found in the case of the thoria powders doped with the other two additives. Nair et al. [18] reported that magnesia, calcia and niobia bring about accelerated sintering in thoria.

In all these investigations cited above, a physical mixture of the dopant oxide and thoria was prepared by milling them together. The powder samples thus obtained were a mixture of two phases viz., thoria and the dopant oxide. During subsequent heat treatment, sintering and the formation of solid solution took place simultaneously. If this method is employed for doping an aliovalent oxide, which is volatile, then the loss of dopant during sintering is inevitable. Moreover Balakrishna et al. [8] observed that the agglomeration of the dopant oxide powders could lead to drastic reduction in densities, especially when the concentration of the dopant oxide is high. Hence, these authors suggested that the co-precipitation procedure would be more suitable for doping niobia in thoria.

Due to the differences in the solubility of thorium oxalate and the oxalates of group VB elements, co-precipitation of these mixed oxalates from an aqueous solution is not possible. For the same reason co-precipitation of thorium and the cations of the group VB elements as hydroxides cannot be carried out as well. It has been demonstrated [11] that the decomposition of the 'mixed citrate complex' of uranium and thorium leads to the formation of solid solutions at low temperatures. Hence, the gel-combustion procedure is an ideal alternative for doping thoria with the oxides of group VB elements. Moreover, the powders obtained by the gel combustion are nanocrystalline and are highly surface active. Therefore, doping thoria through gel combustion would yield homogeneously doped nanocrystalline powders, which would exhibit accelerated sintering.

However, no investigation has so far been reported in which the systematics of doping group VB cations in thoria through gel combustion was studied. Hence, in this study the effect of doping the cations of group VB in thoria on the properties of the latter was investigated. Chandramouli et al. [9,10,15] examined the suitability of various combustion fuels such as polyvinyl alcohol, urea and citric acid for the gel-combustion synthesis of thoria. Citric acid was found the most suitable combustion fuel for the preparation of thoria. Hence in the present work citric acid was chosen as the fuel for the combustion syntheses of the doped thoria powders.

2. Experimental

2.1. Chemicals

Nuclear grade thorium nitrate was supplied by M/s. Indian Rare Earths Ltd., Mumbai, India. Niobium was supplied by M/s. Nuclear Fuel Complex, India, in the form of chips. Thin sheets of tantalum metal were obtained from M/s. Metallwerk Plansee GmbH, Austria. Citric acid (AR grade) was supplied by M/s. Fischer Inorganics and Aromatics Ltd., Chennai, India. Ammonium metavanadate (AR grade) was supplied by M/s. Loba Chemie, Germany. Nitric acid (AR grade) and hydrofluoric acid (AR grade) were supplied by M/s. E. Merck (India) Ltd., Mumbai, India.

2.2. Experimental procedure

In order to prepare the combustion mixture, about 54 g of thorium nitrate was dissolved along with a known quantity of citric acid in about 50 ml of distilled water. A solution containing an appropriate quantity of the dopant cation was added to the above mixture. The quantity of citric acid was so chosen that the ratio of the number of moles of citric acid to that of the total nitrate in the combustion mixture was unity.

In order to dope vanadium oxide, a solution containing the required amount of vanadium was prepared by dissolving ammonium metavanadate in 8 M nitric acid. A solution containing a known quantity of either niobium or tantalum was prepared by dissolving the respective metal in a mixture of acids. These dissolutions were carried out in a beaker made out of polytetrafluoroethylene. An acid mixture comprising two parts of hydrofluoric acid and one part of nitric acid by volume, was used for the dissolution of niobium while an acid mixture that consisted of equal volumes of hydrofluoric acid, nitric acid and water was used for the dissolution of tantalum. Subsequent to the complete dissolution of pieces of these metals, the volume of the solution was brought to a minimum by evaporation.

The aqueous solution containing thorium nitrate, citric acid and the dopant cation was warmed on a hot plate, allowed to gelate, dried and was finally burnt. The 'as-prepared' powder left behind after the completion of the combustion reaction was calcined in air at 923 K for 4 h, in order to remove the residual carbon.

The calcined powder was compacted into pellets having a diameter of about 10 mm and a thickness of about 2–3 mm. The compaction was carried out in a die lined with tungsten carbide by using punches made out of tungsten carbide. An automated double action hydraulic press supplied by M/s. Bemco Ltd., India, was used for compaction. A compaction pressure of 120 MPa, was employed in all these experiments.

The green compacts were sintered in air at temperatures varying from 1173 to 1623 K. A furnace equipped with molybdenum di-silicide heating elements (M/s. Carbolite, UK), was used for carrying out these sintering experiments. During sintering, the temperature was raised up to the desired value at the rate of 300 $\mathrm{K\,h^{-1}}$. Sintering was allowed to proceed for 4 h. Subsequently, the samples were cooled at the rate of 300 $\mathrm{K\,h^{-1}}$.

2.3. Characterisation of starting materials, powders and compacts

The impurities present in the thorium nitrate used in the present investigation were analysed by using an inductively coupled plasma mass spectrometer, model Elan 250, supplied by M/s. Sciex, Toronto, Canada.

The completion of the combustion synthesis was ascertained by quantitative IR spectroscopy using a Bomem MB 100 (Canada) Fourier transform infrared spectrometer. The surface area of the powders was measured by the BET method using a Monosorb-16 surface area analyser supplied by M/s. Quantachrome Inc., USA. The particle size analysis was carried out by using Mastersizer, a particle size analyser supplied by M/s. Malvern, Worcestershire, UK. The X-ray powder diffraction patterns were obtained using an X-ray diffractometer (XPERT MPD system) supplied by M/s. Philips, The Netherlands. The average crystallite size of the powders was measured by the X-ray line broadening technique by the Scherrer formula using the profiles of the (2 2 0) peak [19]. The instrumental broadening was obtained using a standard silicon sample.

The densities of the compacts were measured by using the liquid immersion method with dibutyl phthalate as the pycnometric liquid.

The residual carbon present in the powders as well as in the sintered pellets, was determined by oxidising these samples in a stream of oxygen. The carbon dioxide thus evolved was measured using an infrared detector.

Some sintered pellets were polished to a surface finish of about 0.3 μm (root mean square). These specimens were thermally etched by holding them for 4 h at a temperature in which these pellets were sintered previously. The microstructures of the pellets were obtained by using a scanning electron microscope (SEM; model no. XL 30 ESEM, TMP, The Netherlands). X-ray microchemical analysis of the pellets was done using a Cameca SX-50 electron probe microanalyser (EPMA). The diameter of the emitted X-ray beam was ≈ 1 μm. The accelerating voltage used was ≈ 20 keV and the crystals used were PET for thorium Mα, vanadium Kα, and niobium Lα, and LiF for tantalum Lα. X-ray patterns were obtained for each sample in selected regions.

3. Results and discussion

3.1. Purity of the starting materials

The metallic impurities, which were present in a typical mixture used for the combustion experiment in this study were <100 ppm. The metallic impurities such as Mg, Ca and Ti that can affect the sinterability of thoria were found to be insignificantly low. Hence, the sinterability of the powders used in the present investigation was influenced only by the powder characteristics as well as the nature and concentration of the dopants.

3.2. The combustion reaction

During the combustion process the gel undergoes dehydration followed by denitration and destruction of citric acid [11]. Addition of a solution containing either niobium or tantalum was not found to alter the course of the combustion reaction. Thoria powders doped with either niobia or tantala, obtained by the combustion reaction were granular, free flowing, fluffy and milky white in colour.

In those experiments in which a solution of ammonium metavanadate was added to the combustion mixture, a progressive colour change was noticed. The combustion mixture, which was colourless to begin with, turned light blue, green and then yellow upon further heating. Moreover, in these experiments the evolution of gases was instantaneous, and these reactions took lesser time. The product obtained by calcining the combustion residue was a soft, dull yellow powder.

It is well known [20] that the aqueous solutions containing V^{5+} cation are colourless, while the aqueous solutions containing VO^{2+} and V^{3+} are blue and green in colour, respectively. Hence, the change in colour during the above reactions can be attributed to the change in the oxidation state of vanadium from +5 to +4 and then to +3 with the attendant oxidation of citric acid. It is also well known that pentavalent vanadium is more oxidising than the pentavalent cations of niobium and tantalum [21]. In view of the above, it can be concluded that the oxidising ability of vanadium is responsible for the faster reaction during the combustion synthesis of the mixtures which contained ammonium metavanadate. However, a similar acceleration was absent in those mixtures that contained pentavalent cations of either niobium or tantalum, because of the lesser effectiveness of the latter in bringing about the oxidation.

The IR spectra of thorium nitrate, citric acid and typical 'as-prepared' powders and a calcined powder doped with 0.1 mol% of the three different dopants are shown in Fig 1. The IR spectra of the 'as-prepared' powders reveal that the citric acid is destroyed completely and the thorium nitrate is completely denitrated

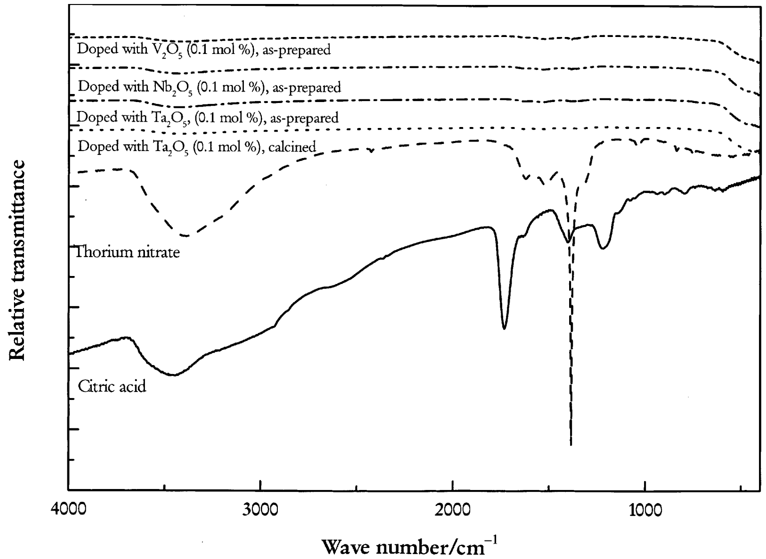

Fig. 1. The IR spectra of 'as-prepared' powders, calcined powders and the reactants.

during combustion. In an earlier study [11], it was reported that a very small peak at 1384 cm^{-1} corresponding to the N–O stretching frequency of the free nitrate was seen in some of the 'as-prepared' samples. However, in the present investigation, such a feature was not observed.

3.3. *Characteristics of the powders*

3.3.1. *Bulk density*

The values of bulk density of the calcined and the 'as-prepared' powders of thoria, obtained in this study are indicated in Table 1. It is evident from Table 1 that for a given dopant, its concentration does not have a significant effect on the bulk density of the thoria powders doped with it. Thoria powders doped with niobia and tantala had similar bulk densities. However, the thoria powders doped with vanadia have a higher bulk density than the former. The higher bulk densities observed with the latter could be attributed to the better packing in these powders, which in turn is due to the morphology and the distribution of sizes in these powders.

3.3.2. *Specific surface area and X-ray crystallite size*

The dependence of the specific surface area of the thoria powders obtained in this study on the concentration of the dopant oxide is indicated in Table 1 and Fig. 2. The specific surface area of pure thoria powders obtained in as many as seven trials with the same batch size, by using the gel-combustion procedure, with citric acid as fuel, reported in the literature [12] are also indicated in this figure. The mean of the values of the specific surface area as well as their standard deviations ($\pm 1\sigma$) reported in Ref. [12] are indicated in Fig. 2 as horizontal lines in order to facilitate easy comparison of this data with the data obtained in the present study.

From Fig. 2 and Table 1, it is evident that doping thoria with either tantala or niobia (up to the extent of 0.5 mol%), does not significantly alter its specific surface area. However, doping thoria with vanadia results in a decrease in the specific surface area. It was also observed that the morphology of the powders doped with niobia and tantala resembled pure thoria derived from gel-combustion, in being granular and porous. However, the thoria powders doped with vanadia were not granular and were less porous. Hence, the latter had a lower surface area than pure thoria derived by combustion synthesis. Experiments carried out earlier in our laboratory [13] indicated that at constant dopant concentration, the total pore volume of the thoria powders doped with niobia and tantala was three times as high as that of thoria powders doped with vanadia.

The X-ray diffraction patterns of the 'as-prepared' powders and the calcined powders did not reveal the presence of any oxide other than thoria. The X-ray crystallite size of the various 'as-prepared' powders synthesised in the present study were in the range of 5–10 nm. The thoria powders obtained by calcining these powders at 973 K in air had typical crystallite sizes in the range of 15–20 nm. The values of the X-ray crystallite size did not show any systematic variation with the concentration of the dopant. The values of the X-ray crystallite sizes obtained in this study for both the 'as-prepared' as well as the calcined powders were comparable to those reported for pure thoria synthesised by gel combustion [10,12].

Table 1
Properties of thoria doped with vanadia, niobia and tantala synthesised by ‘gel combustion’

Sample name	Composition (mol% M_2O_5)	Bulk density ($Mg\,m^{-3}$)		Specific surface area ($m^2\,g^{-1}$)		Carbon content (ppm)	
		AP	CP	AP	CP	AP	CP
Thoria doped with vanadia							
VA1	0.01398	1.23	1.49	17.53	6.19	9481	827
VA2	0.01857	1.18	1.66	13.01	2.85	3943	383
VB1	0.0529	–	1.66	12.97	3.80	–	575
VB2	0.0499	1.46	1.71	–	3.08	10098	801
VC1	0.1273	1.27	–	19.11	8.61	9888	615
VC2	0.1046	1.26	1.41	10.88	4.10	7427	882
VD1	0.2590	–	1.55	26.12	10.45		742
VD2	0.2522	1.02	1.29	11.80	4.90	7991	371
VE1	0.5325	1.12	1.71	29.52	7.23	7703	423
VE2	0.5048	1.03	–	15.05	–	5403	–
Thoria doped with niobia							
NA1	0.0746	0.92	1.23	24.3	16.5	5812	648
NA2	0.1120	0.97	1.34	–	10.5	4582	513
NB1	0.2353	1.06	1.13	19.0	14.1	7593	687
NB2	0.2542	1.21	1.19	–	12.0	8280	579
NC1	0.4921	1.10	1.09	22.0	12.9	6921	682
NC2	0.5128	0.99	1.34	–	11.6	4130	571
Thoria doped with tantala							
TA1	0.1150	1.05	1.22	20.3	13.0	4392	782
TA2	0.1029	1.05	1.31	–	10.6	8894	624
TB1	0.2493	1.02	1.26	25.10	21.44	3854	1043
TB2	0.2553	0.97	1.17	–	9.17	3448	784
TC1	0.5061	1.10	1.26	29.52	15.84	4470	434
TC2	0.5057	1.12	1.33	–	11.98	8289	547
Pure thoria (gel-combustion derived [12]*)*							
–	–	–	–		12.76 ± 0.85	–	1535 ± 0.02

AP = ‘as-prepared’ powder; CP = calcined powder.

3.3.3. Residual carbon

The ‘as-prepared’ powders had a typical residual carbon content of about 5000–8000 ppm while the calcined powders had a residual carbon content of about 500–1000 ppm. The residual carbon present in the thoria powders obtained in the present study are slightly lower than that of pure combustion derived thoria [10,12]. Even though the residual carbon content did not show a systematic decrease with an increase in the concentration of the dopant, the addition of these dopants did catalyse the removal of residual carbon in thoria.

3.3.4. Particle size distribution

The particle size distribution in the ‘as-prepared’ powders, as well as the calcined powders synthesised in this study is given in Table 2. The relative distribution of the constituent particles in the thoria powders doped with vanadia are depicted in Fig. 3.

From Fig. 3 and Table 2 it is evident that the particle size distribution in combustion derived thoria doped with vanadia undergoes significant changes when the vanadium concentration is varied. The distribution is essentially ‘unimodal’ for vanadium concentrations below 0.1 mol%. However, the fraction of particles with a size <100 μm increases with the vanadia content. The powders containing 0.25 and 0.5 mol% vanadia show a polymodal distribution with an increase in the fraction of powders with diameter <100 μm. These observations can be rationalised as follows. An increase in the vanadium content accelerates the combustion reaction, releases the gases at a faster rate, disperses the gel and facilitates the reduction in the mean size of the residue. Upon calcination, this finely divided residue leaves behind a soft powder. The dispersion of the gel increases with the vanadium concentration. Thus, the powders doped with 0.25 and 0.50 mol% vanadia are derived from a more finely divided residue and thus, have a higher fraction of the fines than the thoria powders doped with lesser amounts of vanadia. Among the powders containing 0.02, 0.05 and 0.1 mol% vanadia,

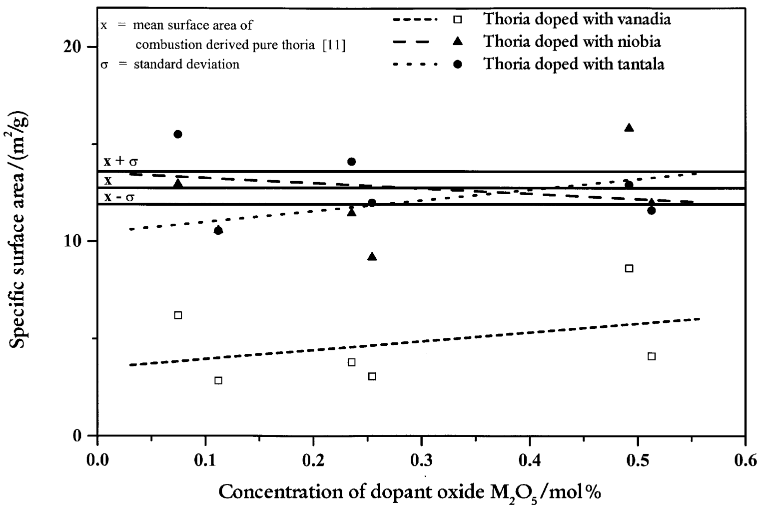

Fig. 2. Dependence of the specific surface area of the calcined powders on the concentration of the dopants.

Table 2
Particle size distribution in calcined powders

	Sample	Particle size distribution (vol.%)		
		10 vol.% of sample has size less than (μm)	50 vol.% of sample has size less than (μm)	90 vol.% of sample has size less than (μm)
Thoria doped with vanadia	VA1	26	79	178
	VB1	24	101	266
	VC1	0.41	90	221
	VD1	0.37	20	155
	VE1	0.29	33	153
Thoria doped with niobia	NA1	23	65	145
	NB1	25	69	156
	NC1	30	92	220
Thoria doped with tantala	TA1	22	68	167
	TB1	24	76	215
	TC1	26	83	209

the particle diameter corresponding to the maximum value of the peak is shifted to higher values with increase in the concentration of vanadia. This is probably due to the pre-sintering of the agglomerates, which increases with the vanadium concentration. However, an increase in this concentration beyond 0.10 mol% does not result in any further shift in the peak maximum. The powders doped with 0.25 and 0.5 mol% vanadia yield an 'as-prepared' residue, which has a higher fraction of the fine particles which are interspersed between the coarser ones. Thus the probability of the increase in the size of a coarse particle by agglomerating with another coarse particle, through pre-sintering, during calcination is diminished. Hence, an increase in the particle size is not found to be significant when the concentration of vanadia is increased from 0.1 to 0.25 and 0.5 mol%.

The particle size distribution in the thoria powders doped with niobia is illustrated in Table 2. These powders exhibit a bimodal distribution with most of the particles having diameters in the range of 50–100 μm. An increase in the concentration of niobia from 0.1 to 0.5 mol%, does not alter the shape of the distribution. However, doping thoria with 0.5 mol% niobia shifts the particle size corresponding to the peak maximum (around 70 μm) to a higher value. This can be attributed to pre-sintering of the agglomerates, which is enhanced by an increase in the concentration of niobia. Ananthasivan et al. [12] observed that thoria powder doped with 2.5 mol% of niobia, derived by gel-combustion, consisted of hard agglomerates. This observation offers additional support to the premise that the addition of niobia aids pre-sintering in thoria during calcination of the combustion residue.

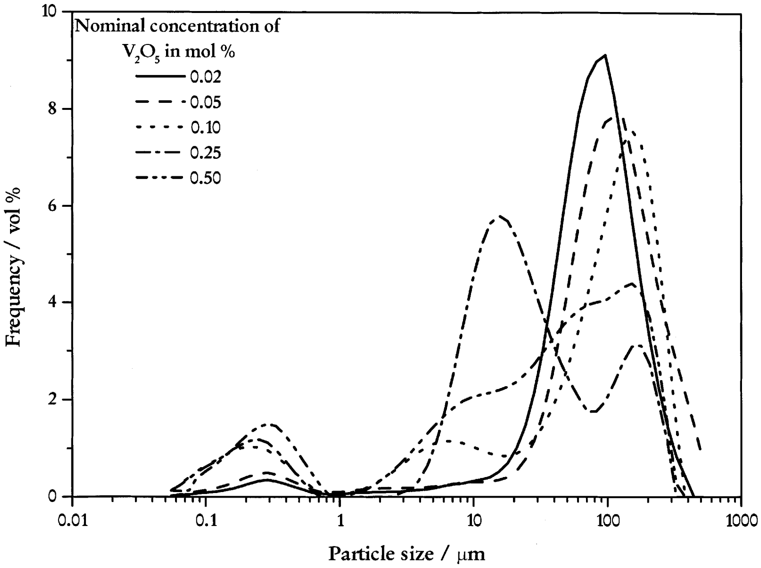

Fig. 3. Dependence of the particle size distribution in calcined powders on the concentration of vanadia.

The size distribution of thoria powders doped with tantala are shown in Table 2. These powders also exhibit a bimodal distribution that is quite similar to that observed for thoria powders doped with niobia. In the powders doped with 0.1 as well as 0.25 mol% tantala, the particle size distribution remains essentially the same. However, when the concentration of tantala is raised to 0.5 mol% the particle size corresponding to the peak maximum (around 70 μm) is found to shift to a higher value. Thus, it can be concluded that the addition of 0.50 mol% tantala facilitates pre-sintering in thoria.

The difference in the nature of the particle size distribution observed in the thoria powders doped with vanadia and the other two dopants (niobia and tantala) arises from the difference in the nature of the combustion reaction. The oxidising ability of vanadium in the aqueous solution influences the size distribution significantly. Consequently, the distribution of particle size in the thoria powders doped with vanadia, shows a systematic variation with the concentration of vanadia. The lack of an oxidising condition in the gels containing niobium and tantalum ions is responsible for the absence of such a systematic variation in the particle size distribution of the thoria powders derived from them.

3.4. Characteristics of the sintered pellets

3.4.1. Sintered density and microstructure in thoria doped with vanadia

The dependence of the sintered density of the thoria powders doped with different amounts of vanadia, on the temperature of sintering are indicated in Fig. 4 and Table 3. The data reveal that the pellets made out of the thoria powders that contain 0.02, 0.05 or 0.1 mol% vanadia, sinter to a density of 9.7 $\mathrm{Mg\,m^{-3}}$ at 1573 K. However, the pellets made out of thoria powders with higher concentrations of vanadia yielded a density in the range of 9.7–9.8 $\mathrm{Mg\,m^{-3}}$, even when they were sintered at temperatures lower than 1573 K.

Chandramouli et al. [10] reported that when the thoria powder, synthesised by gel combustion using citric acid as fuel, was sintered at 1573 K a density of 9.6 $\mathrm{Mg\,m^{-3}}$ could be obtained. Further, these authors also observed that an increase in the sintering temperature by about 100 K, did not cause any significant improvement of the sintered density. By comparing the results reported in Ref. [10] with those obtained in the present investigation, it can be concluded that sintering of nanocrystalline thoria, derived by gel-combustion, is enhanced by the addition of vanadia. Balakrishna et al. [7] observed that thoria powders mixed with 0.25 mol% vanadia could be sintered only to a density of 8.67 $\mathrm{Mg\,m^{-3}}$ at 1423 K.

Even though the addition of vanadia to thoria is found to accelerate the sintering process, those thoria pellets that contained 0.25 and 0.50 mol% vanadia, showed signs of melting when sintered at temperatures above 1473 and 1223 K, respectively. These pellets were also substantially deformed. The alumina boats which were used for sintering of these pellets were coated with a yellow deposit. The SEM micrograph of sintered pellets of thoria containing 0.5 mol% vanadia is shown in Fig 5. From this figure, it is evident that the surface of this pellet has substantial porosity. The results obtained in an earlier study [13] indicated that the pellets obtained by sintering thoria doped with 0.5 mol% vanadia at

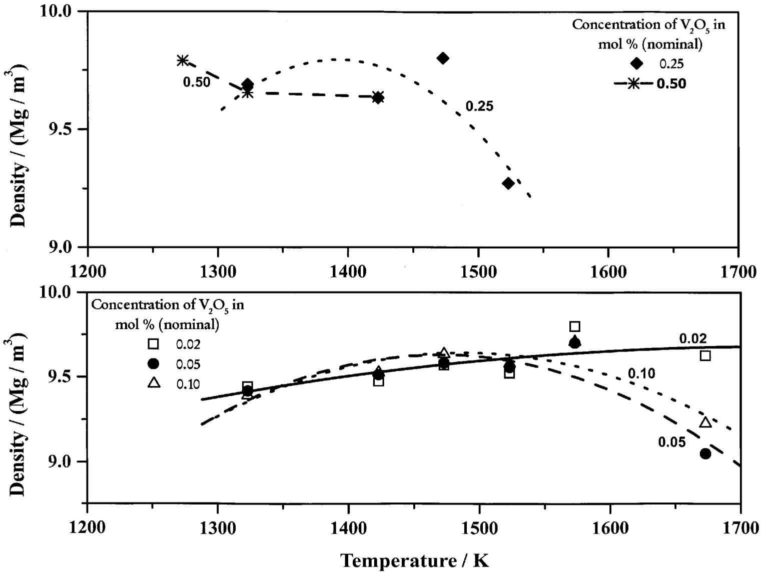

Fig. 4. Variation of the density of the sintered compacts with sintering temperature in thoria doped with vanadia.

Table 3
Sintered densities and carbon content in sintered pellets of thoria doped with vanadia

Sample name	Temperature (K)	Sintered density (Mg m^{-3})	Carbon content (ppm)
VA1	1323	9.44	216
	1423	9.48	284
	1473	9.57	374
	1523	9.52	222
VA2	1573	9.80	85
	1673	9.63	57
VB1	1323	9.42	217
	1423	9.51	283
	1473	9.58	265
	1523	9.56	220
VB2	1573	9.70	85
	1673	9.05	45
VC1	1323	9.39	170
	1423	9.53	219
	1473	9.64	135
	1523	9.58	71
VC2	1573	9.71	99
	1673	9.23	96
VD1	1323	9.69	67
	1423	9.64	97
	1473	9.80	85
	1523	9.27	44
VE1	1273	9.79	–
	1323	9.66	72
	1423	9.64	70

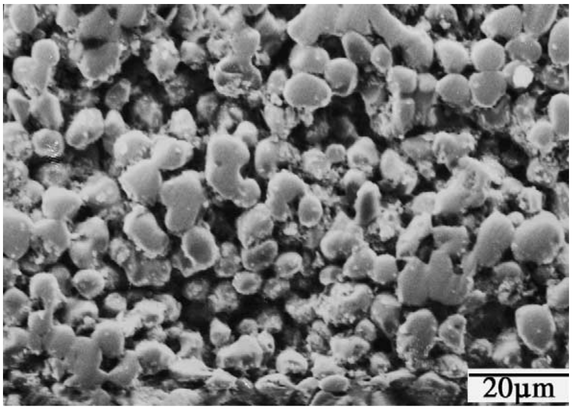

Fig. 5. Ceramograph of thoria doped with 0.5 mol% V_2O_5, sintered at 1423 K. SEM micrograph.

temperatures higher than 1323 K showed substantial reduction in density. In addition it was also reported that these pellets exhibited more defects and blistering and were deformed. Our results confirm the observations made by Radhakrishnan [13]. All the observations made in the present investigation suggest that a liquid phase appeared during sintering beyond the solidus temperature. The physical defects found in these pellets were probably caused by the loss of material due to preferential vapourisation of vanadia from the solid solution or due to the vapourisation of a ternary oxide that was rich in vanadia. In the pellets obtained by sintering thoria doped with 0.10 and 0.05 mol% vanadia, a reduction in the sintered densities was observed at temperatures above 1623 K. However, pellets made out of thoria containing 0.02 mol% vanadia showed a continuous increase in density up to 1673 K.

The SEM images of sintered thoria containing 0.25 mol% vanadia is illustrated in Fig. 6. This microstructure is quite similar to those reported by Chandramouli [15]. Those pellets, which exhibited maximum densification in a given batch, were also found to be translucent. During the microscopic examination of these pellets, which had a thickness of about 2 mm, a diffused image of the beam of light from the source of illumination could be observed on the opposite side.

From the foregoing observations the following conclusions can be drawn. Vanadia when doped in thoria brings about accelerated sintering. Physical defects dominate when the sintering temperature exceeds the solidus temperature of the sample.

A pellet prepared from thoria doped with 0.5 mol% vanadia was examined by EPMA. This analysis, revealed that the segregation of vanadia or 'a ternary oxide phase', rich in vanadium, was absent, in this sample. Since such a segregation was not observed even in this sample which had the highest concentration of vanadia, it is quite unlikely that segregation would have occurred in the other samples which contained <0.5 mol% vanadia. Information on the solubility of V_2O_5 in thoria is not available in the literature. The results obtained in the EPMA investigation mentioned above indicate that the solubility of V_2O_5 in thoria is higher than 0.5 mol% at 1423 K.

Information on the pseudo-binary phase diagram of the system ThO_2–V_2O_5 is not available in the literature. Owing to the dissimilar crystal structures of thoria and V_2O_5 and the large differences in the ionic radii of thorium and pentavalent vanadium, substantial solid solubility of vanadia in thoria is quite unlikely. More data on the ternary oxide phases in this system, as well as information on the solid–liquid transformation temperatures are necessary, to substantiate the above observations. Efforts were made in order to measure the solidus temperatures in these samples by using differential thermal analysis (DTA). However, owing probably to the low heat effects at the solidus temperature, discernible peaks could not be obtained in the DTA of these samples.

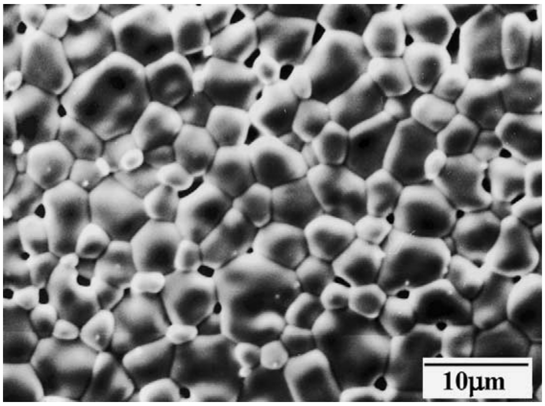

Fig. 6. SEM micrograph of a sintered pellet of thoria doped with 0.25 mol% V_2O_5 sintered at 1573 K.

From the phase diagram data on the V–O system, [23], it is clear that V_2O_5 melts in air at 958 K. Thus, when V_2O_5 is added to thoria by physical mixing, even at temperatures as low as 1423 K a liquid phase would be formed. Subsequently, this molten oxide would dissolve in the thoria matrix. From the vapour pressure data of V_2O_5 given by Knacke et al. [24], it is clear that material loss due to vapourisation would be appreciable if this oxide is heated to temperatures above 1000 K. In view of the above, it can be concluded that the lower densities obtained by Balakrishna et al. [7], for thoria doped with V_2O_5 through physical blending, were caused by the material loss from the pellets due to vapourisation of vanadia or a phase rich in vanadium. The gel combustion derived thoria powders doped with vanadia employed in this work consisted of a solid solution of vanadia in thoria. Hence, preferential loss of vanadia was not significant, especially when the concentration of vanadia was below 0.10 mol%, and accelerated sintering was observed in these powders. However, at higher concentrations of vanadia and at higher temperatures of sintering, loss due to evaporation was found to introduce physical defects in the pellets.

3.4.2. Sintered density and microstructure in thoria doped with niobia

The dependence of the sintered density of thoria powders doped with different amounts of niobia on the temperature of sintering is indicated in Table 4. Comparison of the data obtained in the present investigation with that reported in Ref. [10] shows that among the three different compositions of niobia employed in the present study, the concentration of 0.5 mol% of niobia is most effective in bringing about accelerated sintering in thoria. Balakrishna et al. [6] obtained a density of 9.76 $Mg\,m^{-3}$, by sintering thoria doped with 0.25 mol% Nb_2O_5 at 1423 K. These authors employed conventional powder metallurgical procedure in their study.

The SEM image of the sintered pellets made out of thoria doped with 0.5 mol% niobia is given in Fig. 7. This figure reveals that the surface porosity in this sintered pellet is less than that observed for pellets made out of thoria doped with 0.5 mol% V_2O_5. The absence of precipitates of a second phase suggests that the segregation of either niobia or a niobium rich ternary oxide was not significant in these samples.

Pellets made out of thoria doped with 0.25 and 0.5 mol% niobia were examined by EPMA. These analyses

Table 4
Sintered densities and carbon content in sintered pellets of thoria doped with niobia

Sample name	Temperature (K)	Sintered density ($Mg\,m^{-3}$)	Carbon content (ppm)
NA1	1323	9.07	551
	1423	9.21	359
	1473	9.36	427
	1523	9.54	186
NA2	1573	9.40	139
	1623	9.41	93
	1673	9.23	95
NB1	1323	9.06	427
	1423	9.33	372
	1473	9.35	116
	1523	9.46	983
NB2	1573	9.42	718
	1623	9.44	287
	1673	9.32	74
NC1	1323	8.94	411
	1423	9.68	116
	1473	9.41	101
	1523	9.46	155
NC2	1573	9.53	100
	1623	9.71	55
	1673	9.37	100

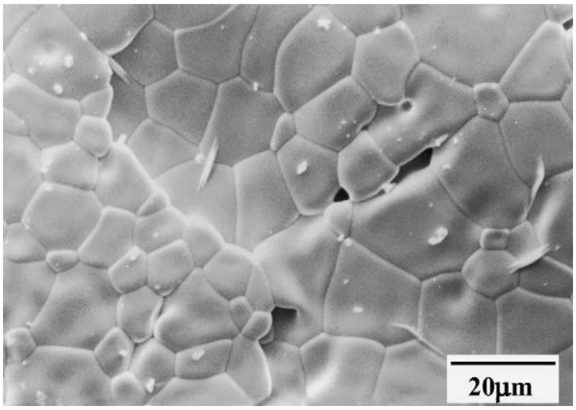

Fig. 7. SEM micrograph of a sintered pellet of thoria doped with 0.5 mol% Nb_2O_5 sintered at 1623 K.

revealed that the amount of niobium present in different regions of these pellets was below the detection limit. The absence of segregation of either niobia or a 'ternary oxide phase', rich in niobium, testified the homogeneous distribution of niobium in the sintered pellets.

Substantial thermal etching was observed when the pellets made of thoria doped with niobia were sintered at temperatures above 1623 K. Further, the photomicrograph of these pellets did indicate enlarged grain boundaries, suggesting the onset of melting. These observations were in agreement with those reported in Ref. [7].

Thoria forms two ternary compounds $ThNb_4O_{12}$ and $Th_2Nb_2O_9$ with niobia [23]. Further in the system Nb_2O_5–ThO_2, the terminal solid solution of niobia in thoria coexists with $Th_2Nb_2O_9$. The eutectic isotherm at 1606 K (27 mol% of niobia) also lies within this two-phase region. Hence, a temperature as high as 1606 K is necessary in order to bring about liquation in thoria doped with niobia. Balakrishna et al. [7] did find evidences of melting, when pellets made out of thoria containing 0.25 mol% niobia, sintered at 1423 K were resintered at 1873 K. The solidus and solvus lines are not shown in Ref. [23]. From the results obtained from the examination of the sintered pellets by EPMA, in the present study, it appears that the terminal solubility of niobia in thoria is higher than 0.5 mol% at 1623 K.

3.4.3. Sintered density and microstructure in thoria doped with tantala

The dependence of the sintered density of thoria powders doped with different amounts of tantala on the temperature of sintering is indicated in Table 5. By comparing the data obtained in the present study with those reported in Ref. [10], it becomes apparent that doping thoria with 0.5 mol% tantala brings down the temperature required to obtain a sintered density of 9.6 $Mg\,m^{-3}$ by about 50 K. Hence, it is evident that the addition of tantala to thoria does accelerate the sintering process. However, the advantage in terms of the reduction in temperature is not as high as in the case of the other two dopants. Balakrishna et al. [7] reported that the thoria powders doped with 0.25 mol% tantala sintered to a density of 7.53–7.6 $Mg\,m^{-3}$ at 1323 K. The absolute values of the sintered densities, obtained in this study in the temperature range of 1323–1673 K, are higher than the density values reported in Ref. [7].

Thermal etching was not predominant in the sintered pellets made out of thoria doped with tantala. The SEM micrograph of a sintered pellet doped with 0.5 mol% tantala is given in Fig. 8. This ceramograph has features that are quite similar to those obtained for gel combustion derived pure thoria [15]. The EPMA investigation of this pellet revealed that the amount of tantalum present in different regions of this pellet was below the detection limit. Thus the homogeneous distribution of tantalum in the sintered pellet was ascertained. Information on the solubility of Ta_2O_5 in thoria is not available in the literature. The result obtained in the EPMA investigation of this pellet indicates that the solubility of Ta_2O_5 in thoria is higher than 0.5 mol% at 1623 K.

Tantalum forms a stable oxide, viz. Ta_2O_5 [24]. The melting point of this compound is 2073 K [25]. Among the oxides (M_2O_5) of the elements that belong to group VB, Ta_2O_5 has the highest melting point. The ionic radii

Table 5
Sintered densities and carbon content in sintered pellets of thoria doped with tantala

Sample name	Temperature (K)	Sintered density ($\mathrm{Mg\,m^{-3}}$)	Carbon content (ppm)
TA1	1323	9.12	435
	1423	9.22	422
	1473	9.32	384
	1523	9.51	254
TA2	1623	9.59	98
	1673	9.29	83
TB1	1323	8.93	471
	1423	9.01	535
	1473	9.42	342
	1523	9.62	188
TB2	1623	9.64	123
	1673	9.38	89
TC1	1323	8.94	551
	1423	9.17	436
	1473	9.32	208
	1523	9.63	231
TC2	1623	9.69	74
	1673	9.39	75

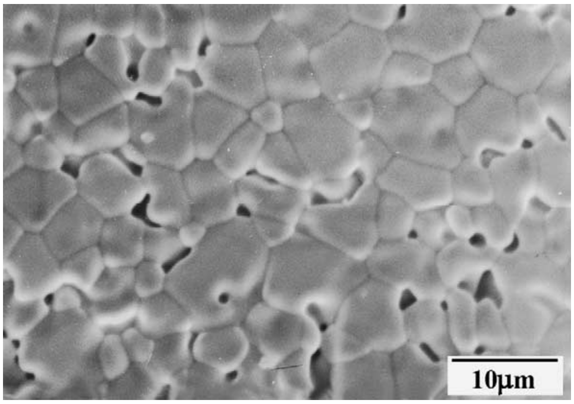

Fig. 8. SEM micrograph of a sintered pellet of thoria doped with 0.5 mol% Ta_2O_5 sintered at 1623 K.

of the pentavalent cations decrease in the following order $Ta^{5+} > Nb^{5+} > V^{5+}$. In view of the above, the ionic mobility of pentavalent tantalum is likely to be lower than that of both V^{5+} as well as Nb^{5+} in the thoria matrix. Therefore, at about 1323 K, the dissolution of tantala in thoria would take place at a slower rate compared to that of either niobia or vanadia. Hence, in the thoria powders doped with tantala by physical mixing, the low ionic mobility of pentavalent tantalum would be responsible for the absence of accelerated sintering. In the thoria powders obtained by the gel combustion route, since homogeneous mixing is ensured down to the ionic scale, formation of solid solution can no longer be hampered by the low ionic mobility of tantalum. However, even in these powders, tantalum does not assist the sintering process as much as niobium or vanadium. This demonstrates that the ionic mobility of the dopant cation plays an important role in bringing about accelerated sintering in thoria. The same conclusion was drawn by Balakrishna et al. [7].

3.4.4. Influence of the method of addition of the dopant, on the sintered density

By comparing the results obtained in the present study with those reported in the literature [6,8], it was established that the method by which the dopant was added to thoria could influence the sintered density of the final product.

Une et al. [26] showed that doping UO_2 with Nb_2O_5 enhances the diffusion of the cations in the host lattice. Further, these authors suggested that the enhancement of the diffusion coefficient of U^{4+} observed when UO_2 is doped with Nb^{4+} or Ti^{4+} is due to the accommodation of the tetravalent dopant cation in the interstitial positions of the lattice. Recently, Song et al. [27] studied the sinterability of compacts made out of a powder which contained a mixture of UO_2, U_3O_8 and 0.5 wt% Nb_2O_5. These compacts were sintered in the temperature range 873–1873 K. The oxygen potential of the gas above these pellets varied from $-470\ \mathrm{kJ\,mol^{-1}}$ (at 873 K) to $-430\ \mathrm{kJ\,mol^{-1}}$ (at 1873 K). These authors observed that in the sintered samples, a niobium rich second phase Nb_2UO_6 was present. Hence, it is quite likely that localised enrichment of niobia can take place, even in thoria samples that are doped with niobia by physical mixing.

During the dissolution of niobia in the thoria matrix, localised concentration gradients would be created. The concentration of niobium across a given grain of thoria would vary with time, during the sintering process, as well. Hence, during the initial stages of sintering the local concentration of niobia near the boundaries of thoria grains would be higher than the overall concentration. It has been demonstrated in the literature [28] that the addition of niobia accelerates the sintering in thoria by creating oxygen interstitials. Hence, a localised increase in the concentration of niobium would lead to an enhancement in defect concentration and assist sintering. Thus, even when the overall concentration of niobia is 0.25 mol%, the local concentration of niobia in the samples prepared by Balakrishna et al. [6] might have been higher than 0.25 mol%. The effectiveness of physical doping would thus depend on both the particle size as well as the degree of homogeneity in the distribution of the dopant oxide. A coarser particle size and an inhomogeneous distribution of the dopant oxide can affect the sintering adversely. Balakrishna et al. [8] observed that the experimentally observed values of the density of the thoria pellets doped with niobia through physical mixing were less than the theoretical densities predicted by both the oxide ion (O^{2-}) interstitial model and the thorium ion (Th^{4+}) vacancy model. These authors [8] attributed the reduction in the density at higher concentrations of niobia to the agglomerated nature of the niobia powder that was used in their study. Hence, these authors [8] suggested the use of a wet chemical procedure for doping niobia, in order to improve the density. When the dopant is added through a wet chemical procedure, homogeneity in mixing is achieved down to the ionic scale. Hence, the concentration of niobia available at the grain boundaries during the initial stages of sintering will be lower than the concentration that prevails in the samples doped with niobia by physical mixing. Alternately, the same density can be achieved by sintering the 'combustion derived' powders at a temperature, which is higher than that required for powders in which niobia is doped through physical means. The data obtained in the present study indicate that thoria doped with 0.1, 0.25 and 0.50 mol% niobia could be sintered to a density of 9.5 $\mathrm{Mg\,m^{-3}}$ at 1523, 1523 and 1423 K, respectively. Thus a raise in the sintering temperature of about 100 K is required for thoria powders doped with 0.10 and 0.25 mol% niobia than those doped with 0.5 mol% niobia. Still there is an advantage of about 50 K in the sintering temperature due to doping thoria with niobia.

A similar mechanism must be operative in thoria powders doped with vanadia and tantala. However, the physical doping procedure does not bring about significant acceleration of the sintering process in these powders. Loss of vanadium bearing species due to vapourisation hampers the densification in the case of thoria powders doped with vanadia by physical mixing, while the lower ionic mobility of tantalum is responsible for the lack of significant acceleration of the sintering process in the thoria powders doped with tantala. However, doping vanadia and tantala in thoria through a wet chemical route does help overcoming these limitations. Thus, accelerated sintering in thoria doped with vanadia as well as tantala could be demonstrated for the first time in this study.

3.4.5. Residual carbon in sintered compacts

The dependence of the amount of carbon residues present in the sintered pellets on the temperature of sintering is given in the Tables 3–5. From these data, it is clear that the residual carbon present in the sintered pellets decreases with an increase in the temperature of sintering as well as with an increase in dopant concentration. However, for the pellets made out of thoria doped with vanadia, the decrease in carbon content with increase in the concentration of vanadia is more marked. This observation can be rationalised if it is assumed that vanadium assists the oxidation of the residual carbon in combustion derived thoria during sintering to a greater extent than both niobia and tantala. It is well known [20,22] that all the three elements belonging to the group VB exhibit multiple oxidation states, varying from +2 to +5. Vanadium has as many as eleven oxides, niobium has three while tantalum forms only the stable pentoxide [24]. Thus, it is evident that vanadium would be more oxidising than either tantalum or niobium owing to the stability of its lower oxidation states. The V^{5+} available in a thoria powder doped with 0.5 mol% vanadia corresponds to about 0.5 wt%. The carbon content in the 'calcined thoria' powder doped with vanadia is <0.1 wt%. Thus an excess of vanadium is present in the matrix which facilitates the oxidation of the residual carbon in thoria.

4. Conclusion

The studies lead to the following conclusions:

1. Thoria powders doped homogeneously with vanadia, niobia and tantala could be obtained using the gel-combustion procedure. All the three dopants bring about pre-sintering in thoria particles during calcination. Among the three dopants vanadia was found to accelerate the combustion reaction. Doping thoria with vanadia was also found to decrease the surface area and increase the bulk density of the calcined thoria powders.

2. Vanadia was found to accelerate the sintering process in thoria. Densities as high as 9.8 $\mathrm{Mg\,m^{-3}}$ could be obtained at temperatures as low as 1273 K, with powders doped with 0.5 mol% vanadia. Formation of a low melting solid solution of vanadia and thoria, and its volatility were found to be the major factors, which caused a reduction in the density when the samples were sintered at higher temperatures. Thermal etching was also significant in these pellets.

3. Niobia was also found to accelerate the sintering process in thoria. However, in order to obtain a density of 9.7 $\mathrm{Mg\,m^{-3}}$, by sintering at 1423 K, thoria had to be doped with 0.5 mol% niobia. A homogeneous distribution of niobium was observed in these samples.

4. Addition of tantala was also found to accelerate the sintering process in thoria. A density as high as 9.7 $\mathrm{Mg\,m^{-3}}$ could be obtained when thoria powders doped with 0.5 mol% tantala were sintered at 1523 K. However, tantala was found to be less effective in bringing about the accelerated sintering in thoria than both niobia and vanadia.

5. It was also demonstrated, that the optimum concentration of the dopant required to cause accelerated sintering in thoria, when the doping is done through a wet chemical route, could be higher than the optimum concentration of the dopant required for conventional powder-metallurgical procedures. It was further demonstrated for the first time that doping of tantala and vanadia in thoria through a wet chemical route brings about significant acceleration of the sintering process.

6. It was also shown that when the doping is done through a wet chemical route, a more homogeneously doped oxide results. Thus, the gel-combustion synthesis is advantageous when the end use calls for a high degree of homogeneity of the distribution of the dopant in thoria.

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