ELSEVIER

Journal of Nuclear Materials 265 (1999) 255–261

journal of nuclear materials

Combustion synthesis of thoria – a feasibility study

V. Chandramouli, S. Anthonysamy, P.R. Vasudeva Rao *

Fuel Chemistry Division, Chemical Group, Indira Gandhi Center for Atomic Research, Kalpakkam, TN 603 102, India

Received 1 September 1998; accepted 2 November 1998

Abstract

In an effort to prepare a thoria powder feed that can be compacted and sintered at lower temperatures, the feasibility of the combustion synthesis was studied. Here, preparations using thorium nitrate as oxidant and urea or citric acid as fuel were studied. The powders thus prepared were characterized for surface area and crystallite size and were compacted into pellets and sintered at 1573 K. The powder and compact surface morphology were studied using scanning electron microscopy. The effect of heating in a microwave oven to carry out the syntheses was studied. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Thoria in the form of dense pellets is used as a blanket material in nuclear reactors. Conventional powder metallurgical methods for the production of dense thoria pellets use temperatures as high as 1900 K during sintering, which is an energy intensive process requiring a sophisticated furnace and extensive cooling system, etc. Balakrishna et al. [1,2] prepared low temperature sintered high density thoria pellets by using niobia as additive. The preparation of thoria and urania–thoria powder feed that can be sintered at lower temperatures without any additives, based on polyvinyl alcohol (PVA) aided denitration of thorium nitrate/uranyl nitrate was reported from our laboratory [3,4].

In recent years combustion synthesis as a preparation method has attracted a good deal of attention. Combustion synthesis also called ‘self-propagating high temperature synthesis’ (SHS) is a novel technique used for the production of a variety of materials ranging from high-tech ceramics to intermetallics [5–12]. The process involves utilisation of the high exothermicity of a chemical reaction between the fuel and the oxidant to energise the synthesis. Usually, combustion of a ‘fuel’ such as urea or citric acid, etc., in air in the presence of a metal salt is used for the synthesis of the corresponding ceramic oxide. The large amounts of gases evolved during the combustion reaction can result in the product to be highly porous. The large exothermicity of the reaction sometimes results in the appearance of a flame whose temperatures can reach in excess of 1000 K. Since the temperatures involved are high, volatile impurities if any, are vaporised resulting in purer products. Thus, the main advantages of combustion synthesis are process simplicity and less energy intensive steps.

Fumo et al. [8,9] and Kingsley and Patil [10] used urea as a fuel for the combustion synthesis of calcium aluminates and iron substituted pervoskites and preparation of alumina and other related oxides. Urea is a cheap and easily available reagent. When combustion of the urea occurs the products are only nitrogen, carbon dioxide and water. Hence, there is no need for subsequent calcination to remove any residue, to obtain pure products. Roy et al. [11] used the sol–gel combustion using citric acid for the synthesis of solid solutions of ultra fine PZT. Schäfer et al. [12] produced YBCO powder using the autoignition of the citrate–nitrate gel. The advantage of using citric acid was that the reaction could be carried out in a controlled manner using simple glassware due to a much less severe exothermic reaction. Dalton et al. [13] used microwave to energize the combustion reaction for the synthesis of carbides, borides, nitrides and silicides of titanium and molybdenum. However, combustion synthesis of the actinide oxides has not been reported. In the present work the feasibility of the combustion synthesis for the preparation of thoria

---

* Corresponding author. Tel.: +91-4114 40 229; fax: +91-4114 40 365; e-mail: vasu@igcar.ernet.in.

0022-3115/99/$ – see front matter © 1999 Elsevier Science B.V. All rights reserved.

PII: S0022-3115(98)00688-6

from thorium nitrate employing urea/citric acid as fuel was studied. Microwave energy was used to ignite the reactants for the preparation of thoria powder feed that can be sintered at a relatively lower temperature.

2. Experimental

2.1. Chemicals

Nuclear grade thorium nitrate was obtained from M/s Indian Rare Earths, Mumbai, India. Urea and citric acid were of Analytical Reagent grade from M/s Sarabhai M. Chemicals, Mumbai, India.

2.2. Experimental procedure

Aqueous solutions of thorium nitrate and urea/citric acid in varying amounts were heated in a microwave oven (frequency 2450 MHz with an output of 600–700 W) till the whole solution was converted into a solid/ powder. The solid/ powder was then transferred into a silica boat and heated for 4 h in air at 1073 K. For the sake of comparison, a few lots were heated over a hotplate and the product obtained was calcined as above. No efforts were made to measure the temperatures of reactions carried out inside the microwave oven.

2.3. Sinterability studies

The sinterability of the thoria powders was determined by measuring the sintered density of the compacts obtained by compacting the calcined powders at 200 MPa into 10 mm diameter pellets (no binder or lubricant was used). The compacts were sintered at 1573, 1673 or 1773 K in static air for 5 h. The density of the sintered pellets was determined using *n*-butyl phthalate as the immersion liquid. The densities reported are the average densities of about 10 pellets.

2.4. Characterisation of the powders

The BET surface area for all the calcined powders was measured by the Nelson and Eggertsen [14] technique using a Surface Area Analyser (Model: Quantasorb Jr., supplied by M/s Quantachrome, Syosset, USA). The particle size analysis was carried out with Mastersizer particle size analyser supplied by M/s Malvern, Wocestershire, UK. The X-ray powder patterns were obtained using a Siemens D 500 X-ray diffractometer employing filtered Cu Kα radiation. The average crystallite size was measured by the X-ray line-broadening technique, from the profiles of the (220) peak. Standard silicon was used for the estimation of the instrumental broadening. The completion of the combustion synthesis was confirmed by infrared (IR) spectroscopic analysis at the required stages by using a Bomem MB 100 Fourier Transform Infrared Spectrometer. Samples of thoria (both powders and pellets) obtained by using urea and citric acid as fuels were analysed by electron microscopy for microstructure and morphological characteristics on a Philips SEM 501 scanning electron microscope. The powder samples were affixed on aluminium disks and were gold coated before microscopic analysis was carried out.

3. Results and discussion

3.1. Combustion synthesis

3.1.1. Synthesis using citric acid

The addition of citric acid to aqueous thorium nitrate solution gives initially a colorless solution. On heating this solution thorium citrate (a white precipitate) is formed [15]. On further heating this precipitate redissolves and froths. Then oxidation of thorium citrate by (nitrate ion) nitric acid occurs giving rise to nitrogen dioxide as one of the gaseous products.

Depending on the citric acid content of the reaction mixture, the reaction was either continuous or a single step reaction in which there was a sudden release of gaseous material. When the citric acid content was less, the evolution of gas was sudden and when it was high, the evolution was continuous over a period of time. The same observation was made by Roy et al. [11] during the synthesis of YBCO.

The product in the case of thoria prepared employing microwave heating was a white porous mass with black or brown craters. The carbon content of the uncalcined product of the microwave derived solid mass was found to be very high −25% in a typical case where citric acid/ NO_3^- was equal to 0.99 (almost stoichiometric). This suggests that thorium citrate has not decomposed at all. This may be due to thorium citrate being transparent to microwaves and also the temperatures attained due to the coupling of other components in the reaction mixture in the microwave oven are not sufficient to ignite the citrate.

The thoria synthesis was completed on a hotplate, giving rise to a gray colored ash that is identified as pure thoria. The carbon content of the hotplate derived ash was only 0.6–0.9%.

When the citric acid content was high, in addition to gaseous evolution some brownish yellow liquid was found to condense on cooler regions of the microwave oven. This may be a mixture of the pyrolytic products of citric acid, namely aconitic acid or citraconic acid.

3.1.2. Synthesis using urea

The synthesis of thoria using urea as fuel, whether it be in the microwave oven or on a hotplate, was always more violent than that with citric acid. When the composition of the mixture is urea rich, the reaction is found to be less violent. The combustion reaction of urea is represented as

$$CO(NH_2)_2 + 1.5O_2 \rightarrow CO_2 + 2H_2O + N_2. \quad (1)$$

The thorium nitrate decomposition is known to be exothermic [16] and the decomposition is represented as

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

However, in the present study, when the urea content was very high (urea/NO_3^- ratio $\geqslant 0.59$) evolution of the reddish brown nitrogen dioxide fumes was not observed. This may be due to the oxidation of urea by nitrogen dioxide formed, at the temperatures prevalent giving rise to nitrogen, carbon dioxide and water as gaseous products. Fumo et al. [8,9] reported nitrogen and oxygen as the gaseous products in the preparation of calcium aluminate and the iron substituted pervoskites by combustion synthesis using urea as fuel. Thus the decomposition of the thorium nitrate in the presence of urea may also be represented as follows:

$$Th(NO_3)_4 \cdot 5H_2O + CO(NH_2)_2 \rightarrow ThO_2 + 3N_2 + 3.5O_2 + 7H_2O + CO_2. \quad (3)$$

When the urea content is high, smell of ammonia is observed and the release of ammonia is confirmed by change in the color of the universal pH paper to pH > 10. The IR spectrum of the uncalcined product of the synthesis always shows the presence of the nitrate at all compositions of the urea/nitrate mixtures. IR spectra of the reaction intermediate (Fig. 1) shows the presence of both nitrate and urea signatures but with no significant change in the positions of the free nitrate. However, there is a slight shift in the carbonyl frequency, which suggests the formation of an intermediate between Th^{4+} and urea via the carbonyl oxygen. The DTA curve of the reaction intermediate of the urea/thorium nitrate mixture, shown in Fig. 2, reveals two endotherms at 350 and 473 K. The endotherms are followed by two exotherms closely placed between 600 and 650 K. The endotherms are due to removal of water and excess ammonia. While the first exotherm may be due to the decomposition of the urea thorium nitrate complex, the other may be due to the redox reaction between ammonia and the nitrate ion.

The above results can be interpreted in terms of a possible mechanism. Firstly, thorium nitrate forms a complex with urea via the carbonyl oxygen. Similar bonding is reported for the case of urea with antimony [17]. Then the complex decomposes to give thoria and ammonia that gets subsequently oxidized by the nitrogen dioxide. The mechanism can be written as

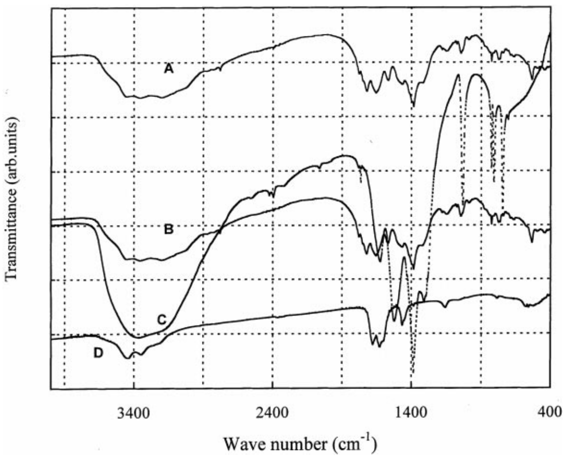

Fig. 1. Infrared spectra of the initial reactants, the reaction intermediate and uncalcined final product of the reaction between thorium nitrate and urea. (A) Reaction intermediate. (B) Uncalcined product of the combustion synthesis. (C) Pure thorium nitrate. (D) Pure urea.

$$Th(NO_3)_4 + xCO(NH_2)_2 + yH_2O \rightarrow Th(NO_3)_4 \cdot xCO(NH_2)_2 \cdot yH_2O, \quad (4)$$

where $x = 4$ or 6 and $y = 4$ or 2, respectively, depending on the method of preparation [18].

On heating further the intermediate decomposes to yield thoria. Typically, the reaction can be written as

$$Th(NO_3)_4 \cdot 4CO(NH_2)_2 \cdot 4H_2O \rightarrow ThO_2 + 4CO_2 + 8NH_3 + 4NO_2 + O_2. \quad (5)$$

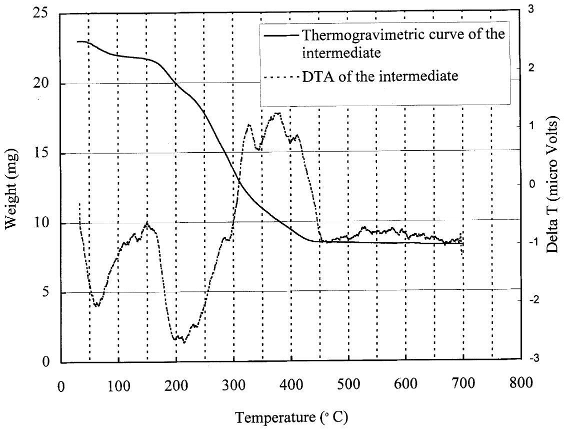

Fig. 2. Thermal analysis curve for the reaction intermediate in the reaction between thorium nitrate and urea.

Finally, the redox reaction Eq. (6) between ammonia and the nitrogen dioxide occurs to give water and nitrogen:

$$2NH_3 + 4NO_2 \rightarrow 3N_2 + 3H_2O + 2O_2. \qquad (6)$$

It was observed in our experiments that the low urea compositions give NO_2 fumes. This may be due to insufficient urea for the complex formation and hence, less amount of ammonia released during decomposition of the intermediate, resulting in an excess nitrate.

3.2. X-ray studies

3.2.1. Thoria obtained from combustion synthesis using citric acid as fuel

In Fig. 3 is given the X-ray patterns of the uncalcined and calcined products of the combustion synthesis using citric acid as fuel employing either hotplate heating or microwave heating. Only the calcined product of microwave decomposed material was crystalline. The hotplate denitrated uncalcined product also showed good crystallinity.

The crystallite size of the uncalcined product of the thoria powder derived by citric acid aided decompostion on a hotplate is 5 nm. The size of the calcined thoria powder from citric acid combustion employing microwave is 11.0 nm. The average particle size measured for the thoria prepared using citric acid was found to be 140 μm. This indicates that the thoria derived using citric acid consists of large aggregate of small crystallites whereas that prepared using urea consists of only loose aggregates.

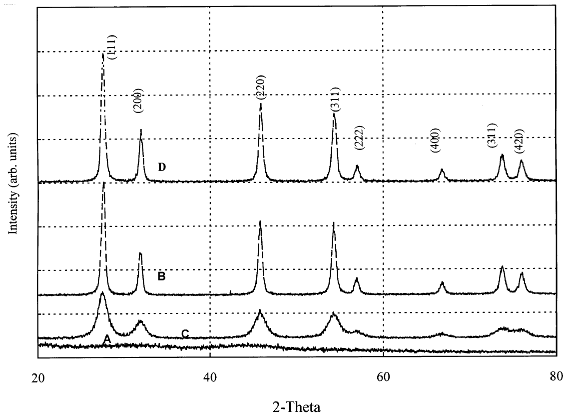

Fig. 3. XRD patterns of the uncalcined and calcined products of the combustion synthesis of thorium dioxide employing citric acid as fuel and microwave oven or hotplate as the heat source. (A) Microwave heated uncalcined product of the synthesis. (B) Microwave heated calcined powder (calcined at 1073 K). (C) Hotplate heated uncalcined powder. (D) Hotplate heated calcined powder (calcined at 1073 K).

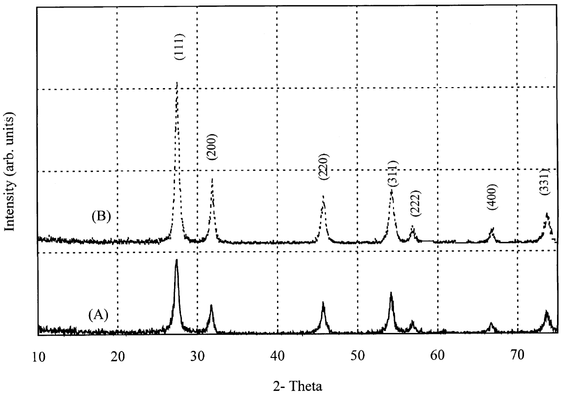

Fig. 4. XRD patterns of the uncalcined and calcined products of the combustion synthesis of thorium dioxide employing urea as fuel and microwave oven as the heat source. (A) Uncalcined product of the synthesis. (B) Calcined powder (calcined at 1073 K).

3.2.2. Thoria obtained from combustion synthesis using urea as fuel

The X-ray pattern of even the uncalcined thoria derived from urea combustion synthesis shows very well-resolved peaks corresponding to thoria. A typical pattern is presented in Fig. 4. The crystallite sizes calculated using the Scherrer formula are 27.3 nm for the uncalcined, urea derived thoria and 33.2 nm for the calcined product. The average particle size of thoria (calcined) obtained by urea combustion is found to be 55 μm.

3.3. Sinterability studies

3.3.1. Sinterability of thoria powder from citric acid

The sintered density of the compacts of powders derived from the combustion synthesis using different amounts of citric acid is listed in Table 1. The specific surface area of the powders is also listed. The surface area remains around 12 $m^2\ g^{-1}$ irrespective of the ratio of the citric acid to nitrate. This is reflected in lower values for the average crystallite size even for the calcined product. The density of the compacts show a clear trend as a function of the initial citric acid/nitrate mole ratio. As the ratio is increased, the density is found to increase. This increase is parabolic. This can be seen in Fig. 5 where the sintered density as a function of the amount of citric acid is plotted. The sintered density showed only a marginal increase with increase in temperature for the microwave produced powders. However, the hotplate derived powders show densities in excess of 95% of the theoretical density even for sintering at 1573 K.

Table 1
Sintered density of pellets of thorium dioxide made from powders prepared using citric acid as fuel in a microwave oven/hotplate

Citric acid/nitrate ratio	Specific surface area (m^2 g^{-1})	Preparation method (microwave oven/hotplate)	Sintering temperature (K)/time	Sintered density (Mg m^{-3})
1.27	–	Microwave oven	1573 / 5 h	9.54 ± 0.05
0.98	15.18	Microwave oven	1573 / 5 h	9.31 ± 0.04
0.64	12.53	Microwave oven	1573 / 5 h	9.23 ± 0.03
0.48	–	Microwave oven	1573 / 5 h	9.19 ± 0.15
0.36	13.06	Microwave oven	1573 / 5 h	8.79 ± 0.06
1.27	–	Hotplate	1573 / 5 h	9.67 ± 0.03
1.01	14.14	Hotplate	1573 / 5 h	9.59 ± 0.03
0.98	14.93	Hotplate	1573 / 5 h	9.44 ± 0.05
0.64	15.18	Hotplate	1573 / 5 h	9.38 ± 0.12
0.495	–	Hotplate	1573 / 5 h	9.61 ± 0.13
0.31	–	Hotplate	1573 / 5 h	9.25 ± 0.13
1.27	13.19	Microwave oven	1673 / 5 h	9.46 ± 0.14
0.99	9.92	Microwave oven	1673 / 5 h	9.23 ± 0.10
0.67	12.3	Microwave oven	1673 / 5 h	9.05 ± 0.12
0.64	12.53	Microwave oven	1673 / 5 h	8.92 ± 0.05
0.36	13.06	Microwave oven	1673 / 5 h	8.48 ± 0.02
1.27	13.19	Microwave oven	1773 / 5 h	9.46 ± 0.04
0.99	9.92	Microwave oven	1773 / 5 h	9.37 ± 0.08
0.67	12.3	Microwave oven	1773 / 5 h	9.15 ± 0.09
0.66	12.09	Microwave oven	1773 / 5 h	9.07 ± 0.12
0.48	13.29	Microwave oven	1773 / 5 h	8.83 ± 0.08
0.32	12.02	Microwave oven	1773 / 5 h	8.77 ± 0.07
0.31	11.33	Microwave oven	1773 / 5 h	8.67 ± 0.05

3.3.2. *Sinterability of thoria powder from urea synthesis*

In Table 2 are listed the sintered density of the compacts and surface area of the calcined powders obtained by using urea as combustion synthesis fuel. The specific surface area of the powders are found to be $\leqslant 1$ m^2 g^{-1}. This is reflected in larger crystallite sizes observed and also sharper XRD peaks. The lower surface area is due to the high temperatures produced due to the redox combustion of nitrate and urea. Fumo et al. [8,9] reported temperatures of 1500 K during the combustion synthesis of calcium aluminates and iron substituted pervoskites using urea as fuel. The density of the compacts is found to be only 88% of the theoretical value of 10.0 Mg m^{-3}. This is to be expected since the surface area of the press feed is low, the driving force for sintering is less. The density does not seem to be affected by the method of heating.

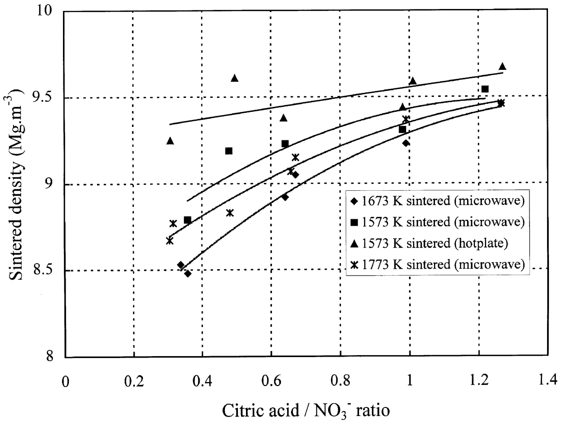

Fig. 5. Plot of sintered density as a function of the citric acid to the nitrate ratio.

3.3.3. *SEM analysis*

The SEM micrographs of the uncalcined and calcined thoria powders obtained by combustion synthesis using citric acid as fuel are shown in Fig. 6(a) and (b). The uncalcined powder aggregate shown in Fig. 6(a) indicates the absence of any discernable surface. Perhaps the sizes of the individual particles are very fine to be seen. Calcining does not seem to improve the surface as seen in Fig. 6(b). Fig. 6(c) and (d) show the SEM of the uncalcined urea derived thoria powders. The uncalcined powder shows a fibrous structure with particles as big as 5 μm.

The micrographs of the surface of the pellets made from the powders obtained by combustion synthesis

Table 2
Sintered density of thorium dioxide pellets made from powders prepared using urea as fuel

Urea/nitrate ratio	Preparation method	Specific surface area ($m^2 g^{-1}$)	Sintering temperature (K)	Sintered density ($Mg m^{-3}$)
3.32	Microwave	3.19	1673 / 5 h	8.55 ± 0.05
1.54	Microwave	1.03	1673 / 4 h	8.55 ± 0.15
0.89	Microwave	0.51	1673 / 5 h	8.58 ± 0.34
0.61	Microwave	0.79	1673 / 4 h	8.59 ± 0.25
3.13	Microwave	3.81	1773 / 5 h	8.76 ± 0.12
1.59	Microwave	0.78	1773 / 5 h	8.41 ± 0.10
0.58	Microwave	1.44	1773 / 5 h	8.86 ± 0.12
0.42	Microwave	0.81	1773 / 5 h	8.99 ± 0.15
1.61	Hotplate	0.83	1673 / 5 h	8.07 ± 0.19
1.01	Hotplate	5.36	1673 / 4 h	8.53 ± 0.23
0.58	Hotplate	0.37	1773 / 5 h	8.69 ± 0.20
3.22	Hotplate	4.54	1773 / 5 h	8.56 ± 0.14

using citric acid and urea are presented in Fig. 7(a) and (b), respectively. The surface of the pellet made from urea derived powder contains uniform spherical grains of ≈2 μm. The surface is highly porous. On the other hand for the pellets made from powders prepared by combustion synthesis using citric acid the grains are large but non-uniform containing very less porosity. The porosity is mostly intragranular. This difference in the

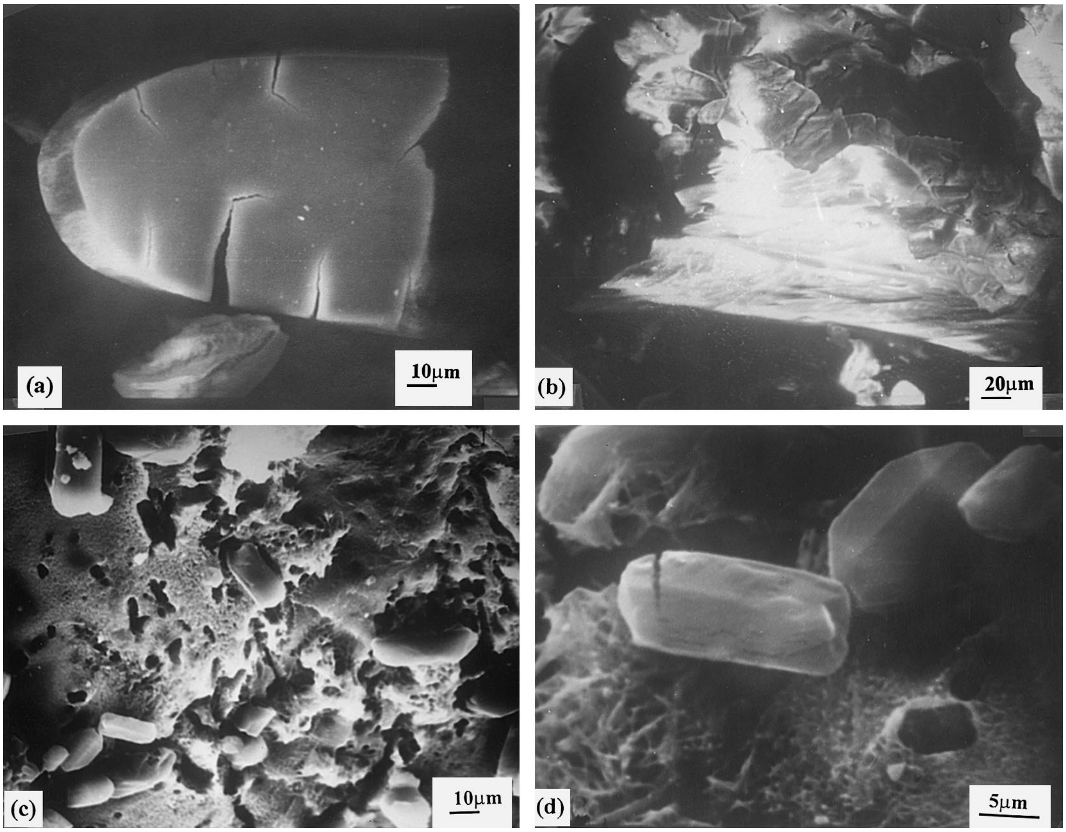

Fig. 6. SEM micrograph of the thoria powder obtained by the combustion synthesis: (a) uncalcined powder obtained using citric acid as fuel on a hotplate; (b) calcined powder obtained by calcining powder in (a) at 1073 K; (c) uncalcined powder obtained using urea as fuel on a hotplate; (d) powder in (c) at a higher magnification showing the fibrous structure.

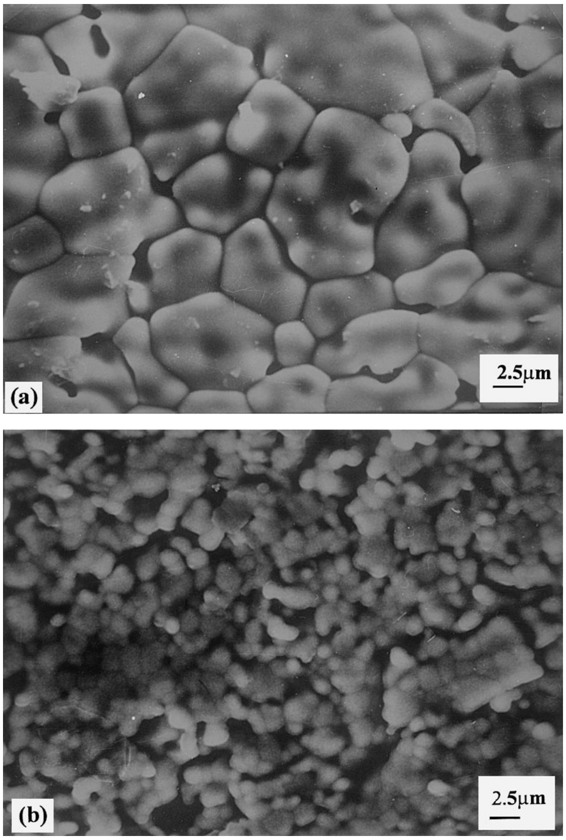

Fig. 7. SEM micrograph of the surface of the thorium dioxide pellet made from powder prepared by combustion synthesis; (a) using citric acid as fuel on a hotplate; (b) using urea in a microwave oven.

morphology can be accounted for by the rather large crystallite size for the urea derived powder but low average aggregate size. The small crystallite size but large particle size of the citric acid derived powder, would definitely improve the sintering behaviour, resulting in high density compacts.

4. Conclusion

The combustion synthesis using citric acid is a potential preparation route that can yield good ceramic grade thoria powder. The microwave heating does not help in the complete combustion of the thorium citrate, while hotplate heating takes the combustion synthesis to completion. The receipe for the synthesis would be to heat aqueous solutions of thorium nitrate and citric acid with a citric acid/nitrate ratio of $\geqslant 1$ preferably on a hotplate. Calcination of the product at 1073 K gives a press feed that can be compacted and sintered at 1573 K to yield a density of at least 94% theoretical density. On the other hand, combustion synthesis using urea always gives a powder low in surface area and hence poor sinterability for the powders.

Acknowledgements

The authors express their sincere gratitude to XRD group, the Spectroscopy group and Mrs Kitheri Joseph all belonging to the Materials Chemistry Division, Chemical Group, IGCAR for recording the XRD patterns, IR spectrum and thermograms, respectively. They acknowledge also the efforts of Mrs Radhika, Metallurgy Division, IGCAR in taking SEM micrographs of various samples.

References

[1] P. Balakrishna, B.P. Varma, T.S. Krishnan, T.R.R. Mohan, P. Ramakrishnan, J. Nucl. Mater. 160 (1988) 88.
[2] P. Balakrishna, B.P. Varma, T.S. Krishnan, T.R.R. Mohan, P. Ramakrishnan, J. Mater. Sci. Lett. 7 (1988) 657.
[3] V. Chandramouli, S. Anthonysamy, P.R. Vasudeva Rao, R. Divakar, D. Sundararaman, J. Nucl. Mater. 231 (1996) 213.
[4] V. Chandramouli, S. Anthonysamy, P.R. Vasudeva Rao, R. Divakar, D. Sundararaman, J. Nucl. Mater 254 (1998) 55.
[5] S.S. Manoharan, K.C. Patil, J. Am. Ceram. Soc. 75 (1992) 1012.
[6] M. Muthuraman, N. Arul Dhas, K.C. Patil, Bull. Mater. Sci. 17 (1994) 977.
[7] T. Ye, Z. Guiwen, Z. Weiping, X. Shangda, Mater. Res. Bull. 32 (1997) 501.
[8] D.A. Fumo, M.R. Morelli, A.M. Segadaes, Mater. Res. Bull. 31 (1996) 1243.
[9] D.A. Fumo, J.R. Jurado, A.M. Segadaes, J.R. Frade, Mater. Res. Bull. 32 (1997) 1459.
[10] J.J. Kingsley, K.C. Patil, Mater. Lett. 6 (1988) 427.
[11] S. Roy, A.D. Sharma, S.N. Roy, H.S. Maiti, J. Mater. Res. 8 (1993) 2761.
[12] J. Schäfer, W. Sigmund, S. Roy, F. Aldinger, J. Mater. Res. 12 (1997) 2518.
[13] R.C. Dalton, I. Ahmad, D.E. Clarke, Ceram. Eng. Sci. Proc. 11 (1990) 1729.
[14] F.M. Nelson, F.T. Eggertsen, Anal. Chem. 30 (1958) 1387.
[15] K.W. Bagnall, in: The Actinide Elements, Elsevier, Amsterdam, 1972, p. 189.
[16] R.N. Tiwari, D.N. Sinha, Ind. Chem. J. 14 (1980) 25.
[17] K.C. Moss, M.A.R. Smith, in: D.B. Sowerby, H.J. Emeleus (Eds.), Inorganic Chemistry of Antimony, Inorganic Chemistry, series 2, Butterworths, London, 1975, p. 253.
[18] D. Brown, in: K.W. Bagnall, H.J. Emeleus (Eds.), Actinide and Lanthanide Nitrates, Inorganic Chemistry, series 2, vol. 7, Butterworths, 1975 p. 145.