

# Synthesis and characterization of nano-structured $\text{Th}_{1-x}\text{Ce}_x\text{O}_2$ mixed oxide

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**Abstract** GEL combustion technique was applied to obtain oxides of thorium and cerium from their respective nitrate solutions using citric acid as the gelating agent. The dried samples were characterized by IR and TG studies. Intermediate and final products during TG studies have been isolated and characterized by XRD studies. All the TG runs during heating of thorium and cerium nitrate with citric acid dried Gels showed a two step process. The weight loss at each step and the X-ray data of the product at each step, helped in suggesting a possible mechanism. Kinetic study was carried out independently for each step. The reaction mechanism as observed during interactive procedure was found to be diffusion controlled. The kinetic parameters (activation energy and pre-exponential factor) for each step in all reactions have been calculated. Observations from XRD studies show that with increase in cerium concentration in the oxides, the lattice parameter values have shown a decreasing trend for all the five compositions studied. It was observed that in TG studies with increase in cerium concentration, the final temperature of the reactions have shown a decreasing trend. SEM studies of the powders reveal that synthesized oxides have a tendency to form agglomerate of varying size ranging

from 50 to 100  $\mu\text{m}$  in case of mixed oxides but the size of thorium oxide powder so synthesized have pore size 10–100  $\mu\text{m}$ . SEM images shows that GEL combustion may result in agglomeration, if the temperature is not properly controlled to the desired value. SEM studies also reveal that each agglomerate contains approximately 10–100 individual particles. Surface area of the mixed oxide powders were determined using Gas adsorption technique. The surface area was found to be in the range of 3–17  $\text{m}^2/\text{g}$  in all cases. Specific surface area of thorium oxide was found to be lesser than cerium oxide but in case of mixed oxides surface area decreases with increase in cerium content. Majority of pores, indicating the particle size are in the range of 0.01–0.04  $\text{cm}^3/\text{g}$ .

**Keywords** Thorium-cerium mixed oxide · Avrami–Eroveef kinetics · Diffusion control mechanism · GEL combustion technique · Scanning electron micrograph · Nano-structures · BET adsorption isotherm

## Introduction

AHWR is an important technological milestone for the third stage of India's nuclear power programme which envisages utilization of thorium and plutonium as a fuel. The 54-rod circular fuel cluster design of AHWR with composite [(Th-<sup>233</sup>U) MOX and (Th–Pu) MOX] fuel with a displacer rod at the center is a very flexible design. Tight packing of the fuel pins offers even distribution of coolant and low local power peaking, which gives sufficient Maximum critical heat flux ratio (MCHFR) margins. In order to maintain even heat flux distribution, it is necessary to make a homogeneously mixed oxide pellets. Preparation of mixed oxide is to be developed which insures uniform

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mixing of the two individual oxides. Cerium has been employed as a mimic to plutonium in this study. These elements are not only isostructural but also have identical cation radii. If the authors compare their oxides it was found that their lattice constants are also very close to each other [1].

A mixture of thorium and plutonium is planned to be used as a fuel in Advanced heavy water reactor (AHWR) and Accelerator driven sub-critical systems (ADSS). The synthetic mixture of thorium and cerium has been prepared and the weight changes during the formation stage have been used to derive kinetic parameters. Method of preparation of nano-structured homogeneously mixed nano particle size powdered mixtures of varying composition were synthesized using GEL entrapment of the metallic ions, followed by heat treatment. Morphology and particle size of the obtained powder were studied using SEM. Surface area of the powder were determined using BET technique. Solid state mixing of individual oxide powders, compacting followed by sintering is conventionally being used. However, the method suffers from the drawback of agglomeration of and low sintering activity, therefore the powders generated by such process need high temperature for sintering, which may be as high as 1600 °C in the case of thoria powder [2]. These problems may be overcome by using various non conventional synthesis methods such as sol-gel, co-precipitation, spray drying, and normal micelle methods.

Many organic complexing agents have been reported in the literature for the preparation of nano structured powders [3–6]. Alinejad et al. [7] have synthesized  $MgAl_2O_4$  using sucrose as a combustion fuel. Chandramouli et al. [7, 8] generated thoria powder to be used as a breeder blanket material by gelation process using Polyvinyl alcohol as gelating agent in a microwave assisted synthesis. Nano crystalline thoria was synthesized by them, using GEL combustion route using citric acid and urea as combustion fuels. Mixed crystals of various proportions of urea thiourea synthesized and characterized using thermogravimetry–differential thermal analysis (TG–DTA) and FTIR spectroscopic analyses by Madhurambal et al. [11]. Kinetics of some

asphalt binders by thermal analysis has been studied by Mothé et al. [10].

## Experimental

### Preparation of dried GEL powder mixtures of Ce(IV)–Th(IV) citrate

Thorium cerium mixed oxide were synthesized by GEL entrapment technique taking cerium and thorium nitrate in various composition as reported in Table 1 using SOL/GEL techniques. Citric acid has been used as the chelating agent. Citrate acts as a chelating agent during drying process and does not allow any of the cations to precipitate prematurely. The whole mass dries as a foamed GEL with cations uniformly distributed over the whole mass (random distribution) statistically. A small portion of the dried GEL powder was used for TGA and IR studies. Rest of the powder was fired in air under controlled conditions carefully and was heated at 1000 °C for 24 h to obtain nano-structured powder of mixed oxides of thorium (IV) and cerium (IV).

### Characterization

IR spectra were recorded on JASCO FT/IR -420 spectrophotometer. DIANO X-Ray diffractometer (copper K- $\alpha$  radiation 1.5431 Å with Nickel filter) was used to record X-ray diffraction patterns.

### Thermal analysis and mechanism

TG was chosen to predict the mechanism of the GEL combustion and to find the combustion temperature. This method has been chosen by Mothé et al. [10] to find kinetic parameters of different asphalt binders.

Calcium oxalate mono hydrate, supplied by NIST was used as a standard reference material for calibration. NETZSCH Model STA 409PC/PG TGA/DTA unit was used for thermal studies. High purity cerium nitrate and

**Table 1** Preparation of citrate GEL mixtures containing varying composition of Ce(III) and Th(IV) in solution

Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O/mL	Th(NO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O/mL	Citric acid/mL	Dried gel powder no.	Th–Ce oxide Sample
0.50	4.50	5.00	S-1	Th <sub>0.9</sub> Ce <sub>0.1</sub> O <sub>2</sub>
1.00	4.00	5.00	S-2	Th <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>2</sub>
1.50	3.50	5.00	S-3	Th <sub>0.7</sub> Ce <sub>0.3</sub> O <sub>2</sub>
2.00	3.00	5.00	S-4	Th <sub>0.6</sub> Ce <sub>0.4</sub> O <sub>2</sub>
2.50	2.50	5.00	S-5	Th <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub>
5.00	0.00	5.00	S-6	Th <sub>0</sub> Ce <sub>1</sub> O <sub>2</sub>
0.00	5.00	5.00	S-7	Th <sub>1</sub> Ce <sub>0</sub> O <sub>2</sub>

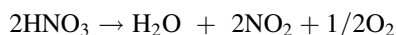
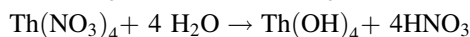
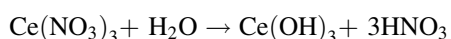
thorium nitrate in different compositions were mixed with citric acid in molar ratio of 1:1. These mixtures were ground in a mortar and pestle so as to obtain fine and uniform powdered mixtures. The process of mixing and grinding was repeated several times. It was observed that the preparation procedure for the reaction mixture had a marked influence on the nature of TG curves.

A small portion of the sample powder from each of seven samples mixtures weighing approximately 10 mg was used for thermal studies. TG were obtained under identical experimental conditions for all the samples. Dry air flow rate of 30 mL/min and heating rate of 5 K/min were maintained while recording the thermo grams of mass loss as a function of time and temperature ranging from ambient to 700 K. TG houses two identical alumina crucibles for the sample and reference. The micro balance works on the principle of null balance technique.

Nitrogen gas adsorption was studied with a view to determine surface area of Th<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub>. Approximately 3 g of the sample powder was used to work out BET adsorption curves for each sample. Adsorption isotherms were generated at a temperature of 77 K. The BET equation is useful in the P/P<sub>0</sub> range of 0.05–0.35. Thus, the isotherm data in this range was fitted to obtain volume of nitrogen required for monolayer adsorption.

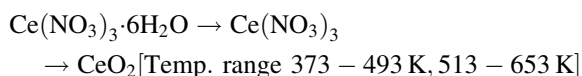
## Results and discussion

IR Spectra of dried gel shows absorption bands due to nitrate (848.5 cm<sup>-1</sup>) and hydroxyl groups (3598.5 cm<sup>-1</sup>) indicating that the nitrates are partially hydrolyzed in the solution. During the process of drying, and GEL formation a network structure of citric acid is formed in which Ce<sup>3+</sup> and Th<sup>4+</sup> ions are trapped. The hydrolysis reactions are as follows:



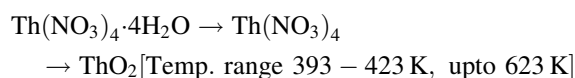
Thermal decomposition of cerium nitrate using TG

The decomposition reaction taking place is represented by the reaction:

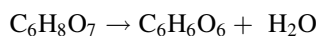


Thermal decomposition of thorium nitrate using TG

The decomposition of thorium nitrate is represented by the following reaction:



Citric acid was used as a chelating agent as it binds with the metallic ions (Ce(III)–Th(IV)), and prohibits the precipitation of solution. Citric acid helps in progress of the reaction. It is also observed that citric acid melts at around 448 K and converts to aconitic acid as per the following equation: (Table 2, 3)



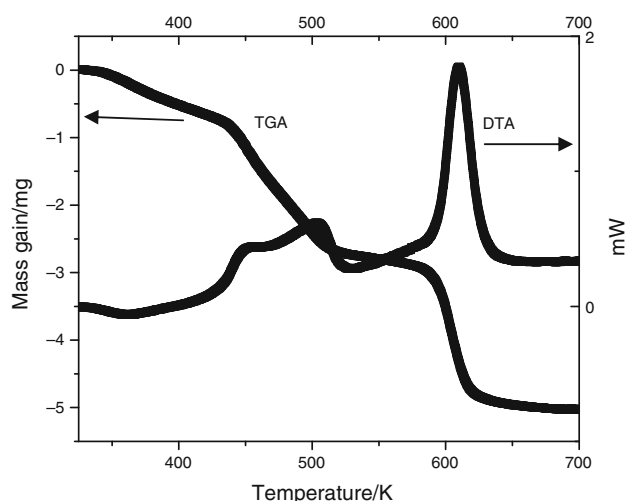
The aconitic acid then converted to itaconic acid as per the following equation:

**Table 2** Residual mass data theoretical and experimental during the TG run of cerium oxide

Steps	Theoretical residual mass/mg	Experimental residual mass/mg	Peak temperature/K
First	8.54	8.11	513
Second	4.28	4.37	653

**Table 3** Residual mass data theoretical and experimental during the TG run of thorium oxide

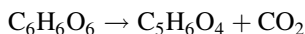
Steps	Theoretical residual mass/mg	Experimental residual mass/mg	Peak temperature/K
First	9.93	10.7	413
Second	5.52	5.41	623



**Fig. 1** TG/DTA curve for sample S-3 obtained at a heating rate of 5 K/min and dry air flow of 30 mL/min

**Table 4** Activation energy, pre exponential factor and expression for rate constants for various steps of thermal decomposition of mixed oxide samples

Sample	Step	Activation energy/KJ/mole	Pre exponential factor	Rate constant
Th <sub>1</sub> Ce <sub>0</sub> O <sub>2</sub>	1st	77.5	$1.53 \times 10^6$	$\ln k = 25.764 - 25603.0/T$
	2nd	211.0	$3.38 \times 10^{15}$	$\ln k = 33.02125 - 26003.48/T$
Th <sub>0</sub> Ce <sub>1</sub> O <sub>2</sub>	1st	32.4	14.30	$\ln k = 1.14002 - 4273.20/T$
	2nd	71.9	$9.89 \times 10^3$	$\ln k = 7.20971 - 9162.08/T$
Th <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub>	1st	128.1	$8.701 \times 10^{12}$	$\ln k = 27.20471 - 15857.89/T$
	2nd	114.2	$2.828 \times 10^7$	$\ln k = 14.8141 - 14293.32/T$
Th <sub>0.6</sub> Ce <sub>0.4</sub> O <sub>2</sub>	1st	66.13	$1.61 \times 10^5$	$\ln k = 9.95 - 8368.39/T$
	2nd	284.8	$8.10 \times 10^{21}$	$\ln k = 47.89 - 35170.89/T$
Th <sub>0.7</sub> Ce <sub>0.3</sub> O <sub>2</sub>	1st	40.30	$1.37 \times 10^2$	$\ln k = 3.49 - 5232.59/T$
	2nd	299.4	$5.096 \times 10^{22}$	$\ln k = 49.12 - 36578.38/T$
Th <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>2</sub>	1st	92.15	$3.59 \times 10^8$	$\ln k = 17.38 - 11514.4/T$
	2nd	143.6	$2.019 \times 10^9$	$\ln k = 18.99 - 17869.6/T$
Th <sub>0.9</sub> Ce <sub>0.1</sub> O <sub>2</sub>	1st	703.3	$3.395 \times 10^{70}$	$\ln k = 151.23 - 82620.5/T$
	2nd	333.3	$3.375 \times 10^{23}$	$\ln k = 50.02 - 40079.2/T$



Itaconic acid form a association complex with Ce<sup>4+</sup> and Th<sup>4+</sup> in acidic solutions leading to GEL formation and entrapment of individual metallic ions.

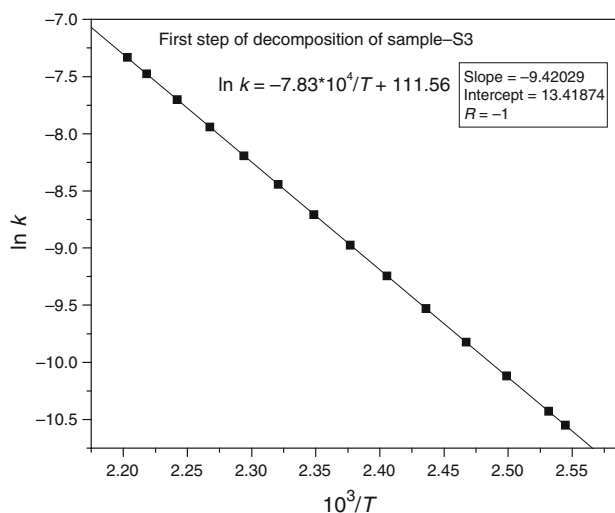
TG studies of dried mixed oxides GEL Samples

TG/DTA combined curves for samples S1–S7 (representative Fig. 1 TG/DTA for Sample S3) indicate that the oxidation reaction of the GEL mixture takes place in two steps. The mass loss data obtained during the first step of TG was found to be Avrami–Erofeev for interfacial reactions for all the samples while data treatment of second step

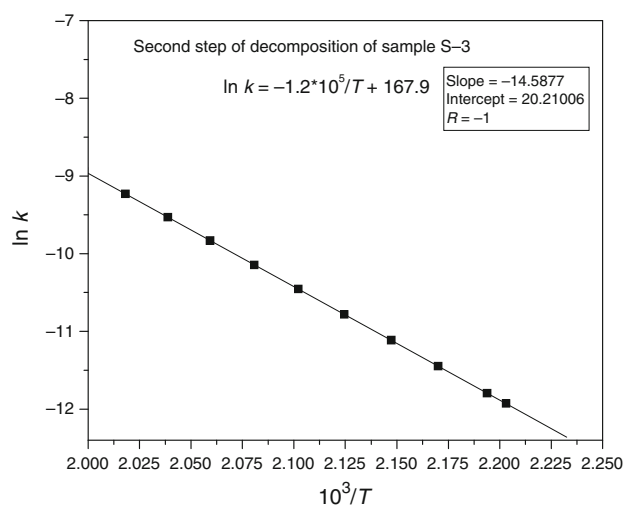
of TG showed that the decomposition is three/two dimensional diffusion control mechanism as suggested by Avrami–Erofeev. The values of rate constants for these steps have been reported in Table 4. The rate constants for first and second order reactions were determined as a function of temperatures, observed fitting (for sample S-3) are shown in Figs. 2 and 3 for first and second steps, respectively.

XRD analysis of the residue left after the TG

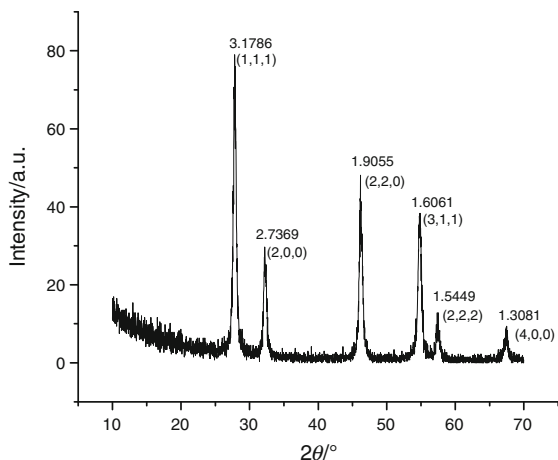
The solid residue left after the TG run were subjected to XRD for product identification and determination of their crystal structures. The XRD pattern of the final product (for



**Fig. 2** Variation of rate constant for the solid state reaction of mixture of sample S-3 in the temperature range of 393–508 K



**Fig. 3** Variation of rate constant for the solid state reaction of mixture of sample S-3 in the temperature range of 553–633 K



**Fig. 4** XRD spectra of the final product Th<sub>0.7</sub>Ce<sub>0.3</sub> O<sub>2</sub> obtained after TGA run of Sample S-3

**Table 5** Variation of lattice parameter ‘a’ with Ce content

Compound	Average a (Å) value	Reference JC-PDF file no.
Th <sub>0.9</sub> Ce <sub>0.1</sub> O <sub>2</sub>	5.65	78-0686
Th <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>2</sub>	5.60	78-0687
Th <sub>0.7</sub> Ce <sub>0.3</sub> O <sub>2</sub>	5.57	78-0693
Th <sub>0.6</sub> Ce <sub>0.4</sub> O <sub>2</sub>	5.43	78-0704
Th <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub>	5.41	78-0691
Th <sub>0</sub> Ce <sub>1</sub> O <sub>2</sub>	5.40	75-0390
Th <sub>1</sub> Ce <sub>0</sub> O <sub>2</sub>	5.30	28-1368

**Table 6** Surface area of different molecule of various gases used for surface area determination

Gas	N <sub>2</sub>	O <sub>2</sub>	Ar	Kr
Area/Å <sup>2</sup> /molecule	16.2	14.1	13.8	19.5

**Table 7** Pore size distribution and their volume contribution in nano structured powder particles of Th<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub> mixed oxide powders

Pore range/Å	Relative volume %						
	Th <sub>1</sub> Ce <sub>0</sub> O <sub>2</sub>	Th <sub>0</sub> Ce <sub>1</sub> O <sub>2</sub>	Th <sub>0.9</sub> Ce <sub>0.1</sub> O <sub>2</sub>	Th <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>2</sub>	Th <sub>0.7</sub> Ce <sub>0.3</sub> O <sub>2</sub>	Th <sub>0.6</sub> Ce <sub>0.4</sub> O <sub>2</sub>	Th <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub>
1000-100	68.05	33.78	17.71	39.00	26.37	55.18	47.30
100-90	0.00	0.00	3.20	0.00	0.00	0.00	5.85
90-80	3.03	1.14	2.58	4.16	3.39	0.00	0.00
80-70	1.73	0.00	0.00	0.00	0.00	2.83	4.28
70-60	0.00	0.70	6.05	7.20	3.34	3.35	3.15
60-50	0.00	0.00	2.78	3.01	3.06	2.46	3.19
50-40	1.74	0.03	10.44	8.66	4.59	6.90	5.35
40-30	7.21	1.37	9.07	7.88	8.53	6.05	3.48
30-20	5.20	57.35	31.71	14.95	48.79	11.33	23.65
20-10	13.03	5.64	16.48	15.13	1.92	11.91	3.75
10-5	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5-3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-0	0.00	0.00	0.00	0.00	0.00	0.00	0.00

each sample) obtained after TG run was recorded (Fig. 4). The peaks obtained toward lower 2θ values are widely separated indicating cubic structure of the product. Secondly, indexing of XRD data indicated that only peaks with miller indices which were all odd or all even were observed. These observations show that the products have FCC structures. Value of lattice parameter ‘a’ was calculated from d values of each peak in XRD (Table 5). The comparison of XRD pattern with those reported for synthesized thorium cerium oxides indicates that the pattern matches with JC-PDF files (Table 5). The lattice parameter shows a decreasing trend as the cerium content increases without causing any distortion in unit cell. These observations are in line with those observed by Mathews et al. [9].

The surface area was determined using following B.E.T. Equation.

$$\frac{x}{(1-x) \cdot V} = \frac{1}{cV_m} + \frac{(c-1)x}{cv_m}$$

$$\text{Slope} = \frac{(c-1)}{cv_m} \text{ and intercept} = \frac{1}{cV_m}$$

From these two equations V<sub>m</sub> can be calculated

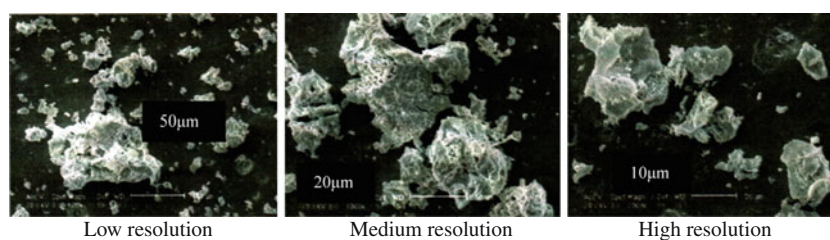
$$\text{Slope} + \text{Intercept} = \frac{(c-1)}{cv_m} + \frac{1}{cV_m} = \frac{1}{cV_m}$$

If one molecule of the gas occupies an area = σ sq cms then the total number of molecules present in the volume V<sub>m</sub> is given by equation

$$S = \sigma v_m \frac{N}{2400} \text{sq. cms.}$$

The areas occupied by molecules of various gases are given in the Table 6. Nitrogen gas adsorption was studied with a view to determine surface area of Th<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub>.

**Fig. 5** SEM image for dried GEL powder of Sample S-5[(Th<sub>0.5</sub>Ce<sub>0.5</sub>)O<sub>2</sub>]



**Table 8** Specific surface area and pore size distribution in Th<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub> powder samples

Samples	Th <sub>1</sub> Ce <sub>0</sub> O <sub>2</sub>	Th <sub>0</sub> Ce <sub>1</sub> O <sub>2</sub>	Th <sub>0.9</sub> Ce <sub>0.1</sub> O <sub>2</sub>	Th <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>2</sub>	Th <sub>0.7</sub> Ce <sub>0.3</sub> O <sub>2</sub>	Th <sub>0.6</sub> Ce <sub>0.4</sub> O <sub>2</sub>	Th <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub>
Specific surface area/m <sup>2</sup> /g	3.3059	6.8096	16.5914	12.8817	11.4799	9.8399	8.7548
Pore specific volume/cm <sup>3</sup> /g	0.01036	0.02464	0.03930	0.03545	0.01681	0.03659	0.02459

Approximately 3 g of the sample powder was used to work out BET adsorption curves for each sample. Adsorption isotherm was generated at a temperature of 77 K. The BET equation is useful in the P/P<sub>0</sub> range of 0.05–0.35. Thus, The isotherm data in this range was fitted to obtain volume of nitrogen required for mono layer adsorption. Table 7 list the pore size range with corresponding volume fraction for each sample. It is clear from the table that major pore volume is due to pore sizes of 1000–100 Å. The pore-specific volume and the surface area of cerium oxide powder was found higher for Cerium oxide as compared to that of thorium oxide powder obtained by this process. The majority of pores in the case of Thorium oxide powder were found to be in the range of 1000–100 Å range while it was only 33.78 in the case of Cerium oxide. The surface area was found to be in the range of 3–17 m<sup>2</sup>/g in all cases (Table 7). It was also observed that the specific surface area of thorium oxide is lesser than cerium oxide but in case of mixed oxides, surface area decreases with increase in cerium content (Table 7). Majority of pores, which are indicating particle size were found in the range of 0.01–0.04 cm<sup>3</sup>/g.

SEM studies of the powders reveal that synthesized powder have a tendency to form agglomerate of varying size ranging from 50 to 100 μm in case of mixed oxides but the size of Thorium oxide powder so synthesized is having 10–50 μm SEM studies also reveal that each agglomerate contains approximately 10–100 individual nano particles (Fig. 5).

## Conclusions

The purpose of this study was to find out the optimum condition for preparation of (Th:Ce)O<sub>2</sub> powder by a GEL combustion technique with subsequent calcination at different temperature and time in air. The GEL combustion technique was found to have several advantages over solid

state reaction route, such as, ease of control, stoichiometry, submicron size particles, and good homogeneity. Intermediates and final products during TG studies have been isolated and characterized by XRD studies. All the TG runs during the heating of Thorium and Cerium nitrate with citric acid dried GELs showed a two step process. The weight loss at each step and the X-ray data of the product at each step, helped in arriving at a possible reaction (Table 8).

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